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Silane Coupling Agents to Reduce Moisture Susceptibility of Asphalt Concrete

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Abstract: This paper describes a study at McMaster University which addressed the effectiveness of silane coupling agents as antistripping agents and their influence on the fatigue properties of asphalt concrete. The main conclusions of the study are:

1. Based on the Japanese Petroleum Institute (JPI) test, treatment of aggregates with silanes improves the compatibility between siliceous aggregates and asphalt cement.
2. Based on the JPI test, surface treatment of coarse aggregates with a silane is more effective than the use of a silane as an asphalt cement additive.
3. Pavebond A.P. and hydrated lime are more effective in improving resistance to stripping than the silane coupling agents.
4. Pavebond A. P. and silane coupling agents reduce the tensile strength of air-cured asphalt concrete - both antistripping agents 'appear' to partially inhibit the development of strong asphalt cement - aggregate bonds.
5. Due to a reduction in tensile strength, an asphalt concrete containing Pavebond A. P. or a silane coupling agent has a shorter fatigue life than an asphalt concrete containing hydrated lime or no additive.

Since silanes appear to reduce the tensile strength of asphalt concrete, their use as an antistripping agent is not recommended.

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SILANE COUPLING AGENTS TO REDUCE MOISTURE SUSCEPTIBILITY OF ASPHALT CONCRETE

1.0 INTRODUCTION

1.1 General

Moisture damage to asphalt concrete is regarded as a serious problem which is often responsible for the premature deterioration of asphalt pavements. The deterioration generally results in decreased serviceability and fatigue life, reduced skid resistance, and increased maintenance and rehabilitation costs. A common procedure for improving an asaphalt concrete's durability with respect to moisture damage is the addition of an antistripping agent to the mix. This report describes a research project which studied the effectiveness of silane coupling agents for improving the asphalt cement-aggregate bond and reducing the moisture susceptibility of asphalt concrete.

At this point it should be noted that there are two basic forms of moisture damage [1]: **Stripping** which involves a separation of the asphalt cement from the aggregate due to the presence of water; and **softening** of the asphalt cement which is responsible for an overall loss of asphalt concrete stability. Although emphasis in this study was on stripping, the reader should keep in mind that the moisture susceptibility tests, which were carried out, do not necessarily distinguish the damage caused by stripping from that due to softening.

1.2 Objectives and Scope

This study was motivated by the reported favourable performance of silane coupling agents as antistripping agents [2,3,4,5] and experimental results which suggest that these agents may also improve resistance to cracking [5] which is related to fatigue failure. The Highway Materials Laboratory at McMaster University coordinated the research programme and implemented the experimental phase. John Emery Geotechnical Engineering Limited (JEGEL) was hired as a subcontractor to complete a literature review [6] and provide some technical assistance for completing the project. ORTECH International was hired as a subcontractor to select suitable silances for the experimental phase of this study [7]. The full reports prepared by JEGEL and ORTECH are provided in Appendices A and B, respectively.

The main objective of the proposed research was to evaluate the effectiveness of silane coupling agents for improving asphalt pavement durability against stripping and for extending fatigue life. The research programme was reduced to performing the following tasks:

1. provide a brief synthesis from the current practice and literature on stripping and the use of silane coupling agents for reducing stripping (completed by JEGEL);
2. select suitable silanes which are compatible with asphalt cement (completed by ORTECH);
3. evaluate the compatibility between asphalt cement and various Ontario aggregates in the presence of antistripping agents using an immersion test;
4. evaluate retained Marshall stability of asphalt concrete mixes where aggregate source and antistripping agent are variables;
5. evaluate fatigue performance of asphalt concrete mixes where aggregate source and antistripping agent are variables; and
6. summarize the study findings and make a statement regarding feasibility of silanes as antistripping agents for asphalt concrete manufactured in Ontario.

Table 1 provides a brief summary of the organization of this study.

TABLE 1

BREAKDOWN OF STUDY COMPONENTS

Step	Study Component and Objectives
1	Gather preliminary information on use of silanes: a) Start literature review to identify progress made with respect to silane application to asphalt concrete (JEGEL). b) Identify potential silane antistripping agents for asphalt concrete (ORTECH).
2	Given information obtained from the previous step, carry out experimental programme (McMaster) to investigate the effect of silane coupling agents on asphalt concrete using: a) Japanese Petroleum Institute Test - Study the improvement, due to the presence of antistripping agents, in the ability of asphalt cement to bond to various coarse aggregates. Establish which procedure is more effective; i.e. surface pretreatment of coarse aggregate with silane or use of silane as an asphalt cement additive. Compare the effectiveness of the silanes to that of existing antistripping agents with respect to improving performance. b) Immersion Marshall Test - Study the improvement, due to the presence of antistripping agents, in retained Marshall stability. Compare the effectiveness of silanes to that of existing antistripping agents with respect to improving performance.
3	Given information from step 2, select the best and worst coarse aggregates to study the effect of silane coupling agents on the fatigue properties of asphalt concrete (McMaster). Compare the effectiveness of silanes to that of existing antistripping agents with respect to improving performance.
4	Finish literature review (JEGEL) and prepare final report (McMaster).

2.0 LITERATURE REVIEW

2.1 General

Stripping involves complex processes which are still not fully understood. Several factors influence the sensitivity of an asphalt concrete mix to stripping: chemical and physical properties of the asphalt cement and aggregate as summarized in Table 2; compacted mix characteristics such as voids mineral aggregate (VMA) and void content; type and volume of traffic; climatic conditions; and the nature of the base [9,10,11]. For this phenomenon to occur, free water must be present.

Most often stripping is related to the aggregate properties. Carbonate aggregates that have dust free surfaces tend to have a better resistance to moisture damage, than aggregates which have a high silica content [9,12]. Although emphasis is most often placed on the stripping of coarse aggregate, the sensitivity of moisture damage to the properties of the fine aggregate must also be considered [2]. In Ontario the stripping problem tends to be regional with the most severe cases reported in the Kingston and northern areas where noncarbonate aggregates such as granite are used [9,11]. No simple correlation between aggregate and asphalt cement chemistries have been established to date [13,14].

It is important to recognize that an asphalt mixture may still be susceptible to moisture damage eventhough all mix components may be chemically and electrostatically compatible [15]. In order to provide the most effective resistance to such damage, good mix design involving compatible materials, good construction procedure and quality control, and proper drainage under the pavement structure are required [3,12]. For more information on factors influencing moisture damage, the reader is referred to References [6,9,10,12,16].

2.2 Signs of Stripping-Related Distress

Although the moisture deterioration of a pavement structure may develop from the top downward, stripping usually starts in the binder coarse [11,12]. It has been found that the damage usually progresses well into the pavement structure before excessive stripping of the coarse aggregate at the bottom, where the damage is usually the severest, is observed [11]. Since the pavement structure is weakened, further damage due to traffic loading accelerates the pavement deterioration. The damage often appears as flushing or bleeding, along with rutting and shoving of the asphalt [11,17,18]. In Ontario, stripping has also been highly correlated to random cracking [11].

2.3 Techniques for Improving Resistance to Moisture Damage

It has already been indicated that good resistance to moisture damage requires the use of good materials and mix design, and proper construction procedure. The VMA should be high enough to provide sufficient binder coating of the aggregate and the air void content should be low enough (2-5%) to ensure a dense mix which adequately resists the penetration of moisture into the asphalt pavement. In regions where good quality aggregates are not available, it is common to use antistripping additives to help reduce stripping. The high cost of transportation generally precludes the practice of importing good quality aggregates from neighbouring regions.

Antistripping agents are usually either applied directly to the aggregate surface or are introduced as an additive to the asphalt cement. Direct application to the aggregate surface has the benefit of concentrating the agent where the problem exists. On the other hand the

addition of chemical additives to asphalt cement, which results in a dilution of the additive where it is required, tends to be more economical.

Many of the commercial chemical additives are based on fatty amines which are surface active compounds [19]. Although these additives improve initial aggregate coating, problems have been identified with some additives including: low heat stability; tendency to promote emulsification which can accelerate stripping at a later stage; and modification of bitumen properties yielding other adverse effects [13,19]. It has also been suggested that the additive and the asphalt cement may in some cases compete for the same adsorption sites on the aggregate surface, thereby reducing the effectiveness of the strong aggregate-attracting asphalt components [2] and, ultimately, the shear strength at the interface [16].

The effectives of an antistripping agent depends on the source of aggregate and asphalt cement [3,17]. The most successful antistripping agent for promoting bonding appears to be hydrated lime [3,20]; see e.g. Table 3. Hydrated lime performs best when applied in a slurrey form as a surface treatment to the aggregate. Unfortunately this application procedure tends to be uneconomical. Although hydrated lime may also be added as a filler, it is not as effective [20]. The amount of hydrated lime required for treatment usually varies between 1-2.5% by weight of aggregate being treated. Fine aggregates, which have greater surface areas, may require more time. Chemical additives, on the other hand are usually introduced at concentrations of 0.3-1.0% by weight of asphalt cement.

2.4 Silane Coupling Agents

Another class of antistripping agents, which appears to have performed well in research laboratories, are silane coupling agents [2,3,4,5]; see, e.g. Table 3. JEGEL [6] reports 13 patents dealing with silane coupling agents. Although positive benefits through the use of silanes have been reported, the literature survey [6] has revealed mixed results in terms of stripping resistance. In general, it has been found that silanes are not effective for all aggregate types. Sanderson's study [2], for example, demonstrated that methylchlorosilanes can have adverse effects when used with carbonate aggregates.

The following sections of this study describe the experimental phase which explored the feasibility of using silane coupling agents as antistripping agents/adhesion promotes for various Ontario aggregates.

TABLE 2

PHYSICAL-CHEMICAL PROPERTIES OF ASPHALT, AGGREGATE, AND MIXTURE INFLUENCING STRIPPING [14]

Materials	Physicochemical Properties
Asphalt	Viscosity Surface tension Volatility Relative fraction polar constituents Phenol group concentrations Carboxylic group concentrations
Aggregate	Size and shape Pore volume and size Surface area Chemical constituents at surface Acidity and alkalinity Adsorption site surface density Surface charge polarity
Asphalt-Aggregate Mixture	Pore space fraction filled with asphalt Asphalt adsorption ratio Chemical constituents of adsorbed asphalt

TABLE 3

EFFECTS OF ANTISTRIP AGENTS ON FREEZE-THAW CYCLE LIFE IN PEDESTAL TEST [3]

Antistrip Agent in Asphalt	Freeze-Thaw Cycle Life*
None	10
0.5% Kling Beta 2550[1]	7
0.5% SC-AT-50[2]	7
0.5% TAA 300[2]	12
0.5% Acra 500[2]	13
0.5% Indulin AS Special[3]	8
0.5% Pavebond LP[4]	12
0.5% BA 2000[4]	29
0.5% Silane A-1120[5]	20
0.2% Lime	16
1.0% Lime	25
2.0% Lime	52

*Notes:

1. AZS; 2. Tomah (Exxon); 3. Westvaco; 4. Carstab; and 5. Union Carbide.

*The higher the number, the more resistant the asphalt mixture has to moisture-related damage.

3.0 LABORATORY TESTING PROGRAMME

3.1 General

Owing to the apparent success of silane coupling agents, an experimental programme was undertaken to determine if silane coupling agents could inhibit the stripping of asphalt concrete containing Ontario aggregates, and to confirm the claim made by Anzaki and Ikeda [5] that silanes may improve the fatigue life of asphalt concrete.

The experimental programme consisted of investigating:

1. bonding of asphalt cement to aggregate in the presence of a silane coupling agent via Japanese Petroleum Institute (JPI) stripping test;
2. retained strength of asphalt mixtures containing a silane coupling agent via the Immersion-Marshall test; and
3. fatigue life of asphalt mixtures containing a silane coupling agent via a repeated-load indirect tensile test.

At each stage of the experimental programme the behaviour of specimens containing a silane coupling agent was compared to that of control specimens which contained no additive, hydrated lime or a commercially available amine-based antistripping agent. This approach allowed the results to be interpreted within a wider context than would have been possible if testing had been completed on the silane-treated mixtures alone.

3.2 Specimen Preparation

3.2.1 Raw Materials

(a) Aggregates

Since the effectiveness of an antistripping agent depends on aggregate surface properties and mineralogy, coarse aggregates from five separate sources were used in the testing programme. This allowed the investigator to take into account the influence that coarse aggregate mineralogy could have on the results. A list of the aggregates used for this study is given in Table 4. The aggregates from Sources A to D were identified by JEGEL and MTO as aggregates with stripping problems. The aggregate from Source E, which was selected as a control aggregate, is a high quality carbonate which was assumed to have a chemistry favourable for developing a good asphalt cement aggregate bond. A standard sieve analysis (ASTM C-136) was performed on each aggregate. The reader is referred to Appendix C for details on the aggregate gradations.

During the testing programme it was found that the fine aggregate component of the asphalt concrete had an important effect on the retained Immersion-Marshall stabilities. As a result fine aggregate from two separate sources, also given in Table 4, were used for the Immersion-Marshall phase of the testing programme. Both fine aggregates are used commercially for manufacturing asphalt concrete.

The combined gradation of the fine (FA) plus coarse aggregates (65/35 proportion) used for the tests on the compacted asphalt concrete are shown in Figure 1. Owing to the gradation of Aggregates A and D, it was not possible to meet the HL4 gradation limits at the 12.5 mm sieve. Since the experimental programme was of a comparative nature, it was decided that the small deviation from specifications was acceptable. It was felt that crushing the coarse aggregate to force the combined gradation to meet specifications could have introduced an additional variable, into the testing programme; i.e. freshly fractured surfaces may be more

susceptible to moisture damage than aged surfaces. Aggregate C was only used for the JPI test since its gradation was not suitable for preparing Marshall briquettes. Besides this aggregate did not display any stripping during the Japanese Petroleum Institute test.

Coarse aggregates A and E together with the Campbellville fine aggregate (FA) were used for the fatigue testing programme. Aggregate A was chosen since it represented an acidic aggregate for which the silanes should have been the most effective for promoting bonding. Aggregate E was used since it represented both a basic aggregate and the control aggregate.

(b) Asphalt Cement

The main bitumen used for this study was a nonblended refinery vacuum tower bottoms asphalt cement which was obtained from Petro-Can through G. Kennepohl of MTO. The source for the asphalt cement, which is designated as Bow River crude, was refined at the Trafalgar Refinery. During the Immersion-Marshall testing phase several specimens were also made using an asphalt cement which was obtained from the storage tank of a local Batch Plant. The reason for using this alternative source was to provide additional data on the influence of the stripping agents on retained Marshall stabilities.

(c) Additives

The list of the additives used for this study and their suppliers is presented in Table 5. Hydrated lime was chosen as a control additive because of the well-documented success of this additive for improving the resistance of an asphalt mixture to stripping [6]. Pavebond A.P., an amine-based, heat-stable additive, was used in order to compare the behaviour of the silane-treated mixtures to that of asphalt mixtures containing a commercially available, MTO approved additive.

Since there are hundreds of silanes which are commercially available, ORTECH was contracted to provide a short list of silanes which would be suitable as coupling agents in asphalt concrete mixtures. Their report on the silane selection is present in its entirety in Appendix B.

Of the five silanes which were recommended, the three which were used for the experimental programme include:

(a) Glymo, an epoxy silane which was also used in the Anzaki and Ideda [5] study;
(b) Damo, a silane coupling agent containing an amine group which has been patented as an aggregate pretreatment additive [2];
(c) Octeo, a silane coupling agent which was selected for this study on the basis of solution compatibility with asphalt cement; see Appendix B.

Since silanes are regarded as mild to severe eye, skin and inhalation irritants, protective mask, gloves and clothing were worn when working with these chemicals.

3.2.2 Proportioning and Specimen Manufacture

(a) Japanese Petroleum Institute (JPI) Test

The Japanese Petroleum Institute (JPI) test, whose procedures are given in Appendix F, was used to determine the compatibility of the Bow river asphalt cement with the various aggregates in the presence of the antistripping agents. This test was chosen since it was considered to be simple and quick to perform, yet sensitive enough to provide information on the compatibility between an asphalt cement and aggregate. All specimens for this test consisted of 10 mm nominal size coarse aggregates which were coated with 5.5 percent, by

weight, asphalt cement. In addition to studying the effect of the antistripping agents on the aggregates, the JPI test was also performed using asphalt-coated glass microscope slides. The pretreated hot slides were coated with 0.05 mm of asphalt cement as described in Reference [13].

The additives were introduced as follows:

i) Hydrated Lime - one percent lime (by weight of aggregate) was applied directly to the surface of the coarse aggregates in the form of a slurrey, which consisted of 30 percent hydrated lime and 70 percent water, as recommended in Reference [20]. The treated aggregate was subsequently allowed to dry in an electric oven at 43°C for 24 hours before being coated with asphalt cement.

ii) Pavebond A.P. - this additive was mixed directly into the asphalt cement (AC) at one percent (by weight of AC) as recommended by the supplier.

iii) Silanes - the silanes were used to pretreat the aggregates at room temperature via a silane-water solution. Two silane-in-water solution concentrations were used, namely 0.5 and 1.0 percent. Each aggregate was soaked in a fresh silane solution for approximately 10 minutes to ensure proper coating of the aggregate and then was placed in an electric oven set at 43°C for 24 hours to dry. It should be noted that the Glymo and Octeo required a pH adjustment of the solution to ensure solution stability; see Appendix B. In addition to using the silanes as an aggregate pretreatment, they were also tested as an asphalt cement additive. The silanes were added, for this group of tests, in concentrations of 0.45 and 0.9 percent (by weight of asphalt cement) directly into the hot asphalt cement.

(b) Immersion-Marshall and Fatigue Specimens

A standard mix design was used for manufacturing all specimens. Each specimen contained 5.5% (by weight of aggregate) asphalt cement. The ratio of coarse to fine aggregate was 35/65. Specimens were manufactured according to MTO LS-281 and LS-283 procedures for Immersion-Marshall and regular Marshall briquettes, respectively. When manufacturing the regular Marshall briquettes, which were used for the fatigue tests, the last three compaction blows were completed using a nonbevelled head to ensure that both faces were parallel.

When using the hydrated lime, only the coarse aggregate was pretreated. The lime and Pavebond concentrations for the asphalt briquette manufacture were one percent by weight of coarse aggregate and one percent by weight of asphalt cement, respectively. For most specimens incorporating silanes, only the coarse aggregate was pretreated with a 3 percent (by weight of coarse aggregate) silane solution which was prepared at a 1 percent silane concentration. Two sets of specimens were manufactured where the fine aggregate was also pretreated with 3 and 9 percent, by weight of fine aggregate, silane solutions. One set of specimens was manufactured with 1 percent (by weight of asphalt cement) Damo being added to the asphalt cement rather than to the aggregate surface. All aggregates, were placed in the oven at 155°C for 24 hours before samples were manufactured.

3.3 Test Procedures

3.3.1 Japanese Petroleum Institute (JPI) Test

As indicated previously, the Japanese Petroleum Institute procedure was adopted for this study for determining the compatibility of the asphalt cement and coarse aggregate; details are given in Appendix D. As with other static immersion tests, the procedure involves immersing the samples of coated aggregated in hot water for a predefined period of time, and

then evaluating the nature of the coating after this period. It was found that the JPI test was simple and quick to perform. The definitions of the patterns for stripping classification are shown in Figure 2. It should be noted that the JPI test was carried out in both fresh water and salt water environments.

3.3.2 Immersion-Marshall Testing

The Immersion-Marshall test was carried out following MTO LS-283 procedures. In addition to determining the retained stabilities, a visual rating of the fractured failure surface of all specimens was carried out. The Immersion-Marshall test was selected for studying resistance to stripping, rather than an advanced indirect tensile test [21,22] due to good experience with this test in Ontario; see e.g. reference [23].

3.3.3 Fatigue Testing

After manufacturing the 100mm diameter briquettes, they were stored overnight at room temperature in the laboratory before being tested on the following day using an indirect tensile stress loading configuration [24,25]. The indirect tensile tests were performed using a MTS closed-loop servo-controlled bydraulic ram system. Testing was completed in two stages for each mix:

1. Three samples were statically broken using the displacement control ram mode in order to establish the average tensile strength. The displacement rate of the loading ram was 50 mm/minute.
2. Samples were then failed under cyclic loading with the same support conditions as used for the static tests, see Figure 3. A load control mode, using a compressive haversine wave at a frequency of 1 Hz, was required to maintain uniform cyclic loading. Specimens were failed in fatigue using either 15 or 30 percent of static failure strength load level. These levels were chosen based on the fatigue life properties of asphalt mixtures reported in Reference [25]. According to Figure 14 of this Reference the fatigue life should lie within the range 100 to 10,000 cycles, depending on the stress ratio.

Unlike the failure mode of Portland cement concrete, asphalt concrete failure is ductile. As a result, the number of cycles to failure is very sensitive to the definition of failure. In this study failure was defined as the point at which the rate of accumulated irrecoverable displacement appeared to accelerate; i.e. identified by Point A in Figure 4. At this stage of the loading history each specimen started to develop a well-defined crack along the vertical diameter of the specimen. It was found that the accumulated irrecoverable displacement at failure δ_f^P, was consistently between 1 and 1.5 mm. For each series of specimens, δ_f^P at failure appeared to be constant.

TABLE 4

SUMMARY OF AGGREGATES USED FOR THE STUDY

(a) Coarse Aggregate

Designation	Source	Remarks
A	Indusmin, Midland	Badgeley Is., quartzite, 100% silica
B	Utehof Quarries, Barrie	upper lift, ultra fine-grained limestone
C	Rama Stone Quarry, Orillia	quartzite microcline feldspar
D	United Aggregates, Gloucester	dolomitic sandstone, 60% sandstone, 40% carbonate
E	Nelson Aggregate Co., Burlington	100% carbonate

(b) Fine Aggregate

Designation	Source	Remarks
FA	Sherman Sand and Gravel Co., Campbellville	siliceous aggregate
FB	TCG Materials Ltd., Aberfoyle	siliceous aggregate

TABLE 5

SUMMARY OF ANTISTRIPPING AGENTS USED FOR THE STUDY

Designation	Source	Remarks
Lime	Beachvilime Ltd. Ingersoll, Ontario	Hydrated Lime
Pavebond A.P.	Morton Thiokol Ltd. Carstab Division Mississauga, Ontario	Amine-based additive
Glymo Damo Octeo	Huls America Inc. Petrarch Systems Briston, PA. 19007	Silane Coupling Agents

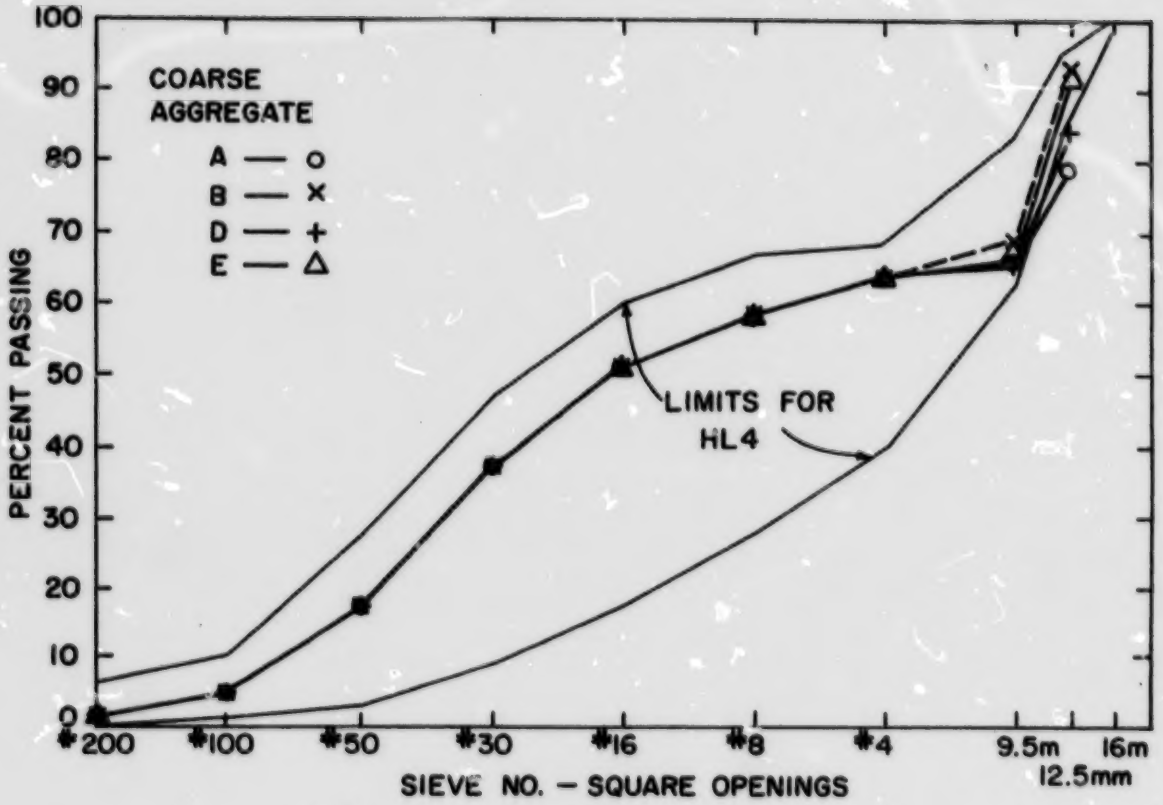


FIGURE 1. Combined gradations of fine and coarse aggregates used for manufacturing briquettes.

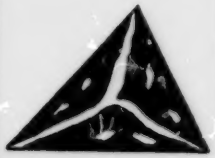
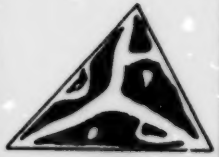
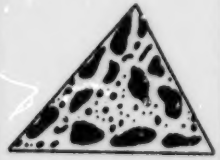
No. of Pattern	I	II	III	IV-1	IV-2
Definition	No stripping occurs. Edges can be light brown.	Stripping on edges and small dot stripping occur.	Stripping on edges widens. Dot stripping occurs.	Continuous stripping occurs.	Asphalt remains in dots.
Appearance					

FIGURE 2. Definition of stripping patterns for JPI test [5].

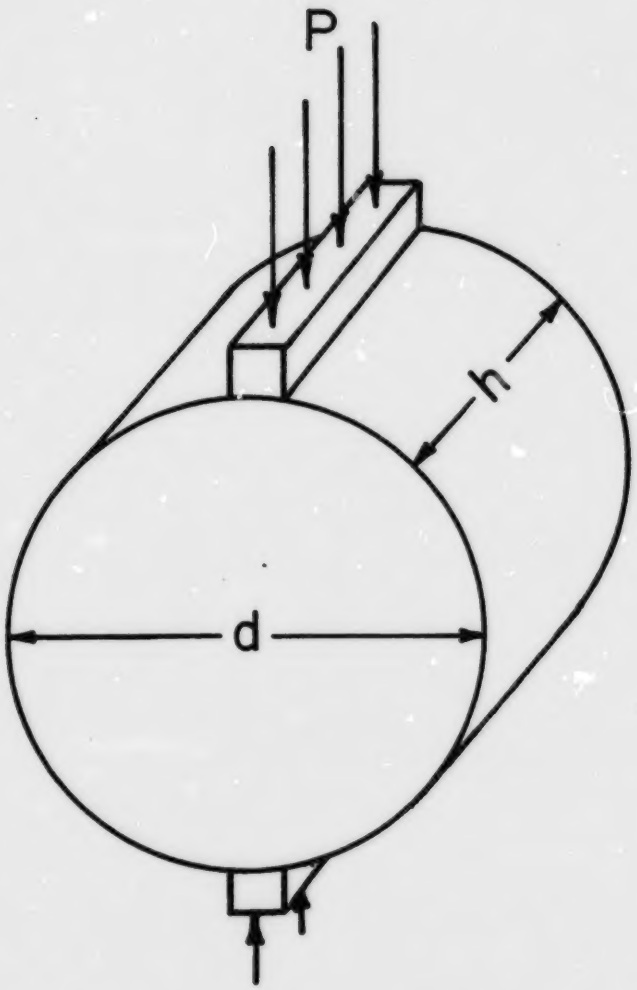


FIGURE 3. Loading configuration for split cylinder tests

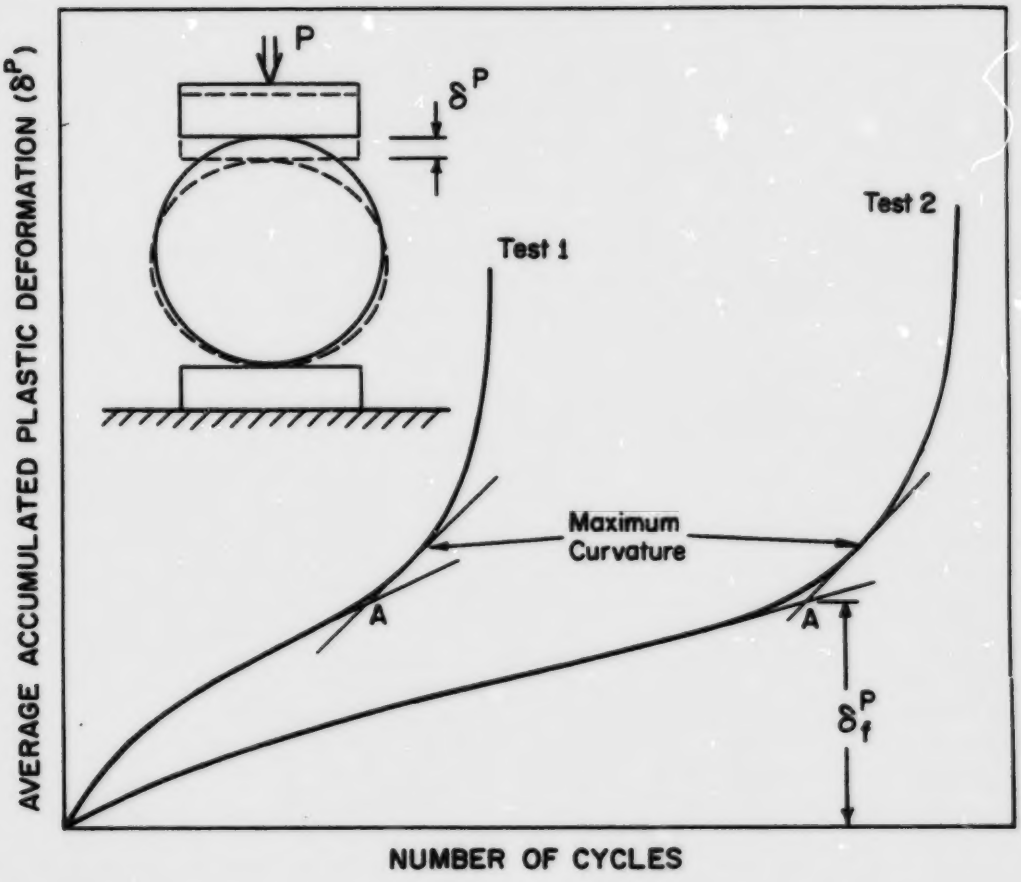


FIGURE 4. Typical deformation history results from fatigue tests (schematic).

4.0 Presentation of Results

4.1 General

Unless indicated otherwise, asphalt concrete mixtures were made using the Bow River asphalt cement and the Campbellville fine aggregate.

4.2 Japanese Petroleum Institute (JPI) Test

One objective, with the Japanese Petroleum Institute Test, was to evaluate the influence of silane addition technique on improving the asphalt cement-aggregate bond. The two procedures which were compared were the aggregate treatment and asphalt additive techniques. Since it was not clear at the beginning of this testing programme how sensitive the stripping resistance would be to the silane concentration, it was decided to carry out the JPI Test using both 0.45 and 0.9% additive concentrations. Using the results of Reference [2], it was estimated that these concentrations would provide a silane concentration at the asphalt cement-aggregate interface of the same order as would be attained when treating the coarse aggregate with 3% (by weight of coarse aggregate) of 1 % silane solution. It should be noted that these levels of silane additive concentration are 10–20 times greater than that which was shown to be effective in Reference [3]. Comparisons were made using only Aggregate A which was expected to undergo the severest stripping and for which the silanes were assumed to be most effective.

The results from the JPI test on the various aggregates and glass slides are summarized in Tables 6 and 7, respectively. Figures 5-7 provide typical appearances of the tested coarse aggregate samples. The asphalt cement tended to collect in small beads on the aggregate surface for samples which displayed stripping as shown in Figure 5. On the other hand aggregates, which did not strip, maintained their uniform asphalt coating throughout the entire test as shown in Figures 6 and 7. It was clear from the results of this test that the silanes were better when used as an aggregate surface treatment than as an asphalt additive. In general, the silanes performed as well as, or better than, the other antistripping agents which are currently used. As anticipated, the tests which were completed in the salt water environment were severer than those using fresh water. Both Glymo and Octeo were better than Damo which has been patented as an asphalt cement additive. The two worst aggregates for stripping were A and D which are highly siliceous. Since nontreated specimens containing Aggregates B and C did not strip, the reported moisture damage of asphalt concrete containing these aggregates must have been due to factors other than binder-aggregate incompatibility.

In order to study the effect of curing environment on the effectiveness of the antistripping agents, the JPI tests were completed on asphalt covered glass slides. One set of slides was cured at 25°C for 70 days whereas the other set was cured at 75°C for 24 hours. These tests indicated that only Damo appeared to be sensitive to the pre-test curing environment, thereby suggesting that Damo might display some instability due to an unfavourable curing environment. Except for Damo, the antistripping agents reduced stripping of asphalt cement from the glass surface. The results from a preliminary set of tests on slides, which were cured only for 24 hours at 25°C, were similar to those of Case A.

Since the surface treatment procedure appeared to reduce stripping more than the additive approach, it was decided to proceed with the rest of the experimental programme using the silanes primarily as a surface treatment rather than as an additive.

4.3 Immersion-Marshall Test

Antistripping agent, and coarse and fine aggregate sources were variables in the Immersion-Marshall testing programme. Representative results from this stage of the experimental programme are summarized in Figures 8 and 9, and in Table 8. More detailed data are provided in Appendix E. The results from this phase of the experimental programme may be summarized as follows:

1. Specimens containing an antistripping agent had higher resistance to moisture damage than those containing no agent. In some cases the increase was very small.
2. Specimens containing silanes did not perform as well as those containing Pavebond A.P. or lime.
3. Pavebond A.P. appeared to be the most effective antistripping agent.
4. Asphalt concrete mixes made with the supposedly better control aggregate (E), did not have better resistance to stripping than those made using other aggregates.
5. Visual inspection of fractured surfaces revealed that the low retained stabilities of most asphalt concrete mixtures were due to the stripping of the fine aggregate and not the coarse aggregate which was treated.
6. An attempt to increase stripping resistance, by treating the fine aggregate with Damo or by adding the silane coupling agent as an asphalt additive rather than as an aggregate surface treatment, decreased the stability of the air-cured specimens by 30 percent (Figure 9). As a result 100% retained stability could only be achieved by a simultaneous reduction to air-cured strength and increase in water-cured specimen strength.
7. Although visual inspection of fractured surfaces revealed considerable fine aggregate stripping, the treatment of fine aggregate increased the Marshall stability of the water-cured specimens very little.

After having established that the fine aggregate was partially responsible for the low retained stabilities, a boiling test was carried out on this aggregate. The boiling test was not successful in revealing a stripping problem with the fine aggregate. During a subsequent series of tests, the Campbellville aggregate was replaced with an alternative fine aggregate, which is also used for commercial production of asphalt cement. The retained stabilities were not improved when the fine aggregate from Campellville was replaced by that from Aberfoyle, see summary of results in Appendix E. Owing to a limited supply of materials it was not possible to further investigate the sensitivity of retained stability to the nature of the fine aggregate or to the level of silane treatment of the fine aggregate.

The retained stabilities appeared to be sensitive to the asphalt cement source. However, owing to the limited data for comparison, conclusions cannot be drawn with respect to the sensitivity of retained stability to asphalt cement source.

The results clearly indicated that silanes may not always be as effective as reported in some of the literature. The findings are, however, consistent with the observations reported in the literature. Sanderson [4], for example, observed that the measured improvement in resistance to stripping is sensitive to the coarse aggregate type used in the test and the type of test performed. He showed that the treatment of limestone with methylchlorosilanes "increased" stripping in wash tests but decreased it in immersion compression tests. In a more recent study carried out in Germany [26], it was observed that, although silanes improved resistance to stripping, the asphalt mixture stability of some air-cured samples can be reduced when adding silane antistripping agents. Such a reduction in stability of air-cured samples was observed in this study; see, e.g. Figures 8 and 9. The reduction in strength for air-cured specimens, where the fine aggregate had also been treated was surprising since the fine aggregate is siliceous and silanes are supposed to be most effective with respect to promoting

bonding between siliceous aggregates and asphalt cement. Although the reason for strength reduction is not clear, it is clear that Damo inhibited the development of a strong asphalt cement-aggregate bond.

Based on the results from this study and those reported elsewhere [6], it is clear that the effectiveness of silanes for decreasing sensitivity to moisture damage depends on the nature of all constituents of the asphalt concrete mixture. Furthermore, the use of an agent to increase stripping resistance can have adverse effects on other properties such as air-cured stability.

4.4 Fatigue Tests

For each set of specimens containing the same antistripping agent, three samples were first tested quasi-statically at a loading displacement rate of 50 mm/min, and then six samples were failed under cyclic loading; three samples were tested at each nominal fatigue level – 15% and 30% of the static strength. These loading levels were selected after reviewing the results given by Adedimila and Kennedy [25] as indicated previously. Their results suggested that failure should occur between 100 and 10,000 cycles for the loading levels which were adopted for this study. Appendix F provides detailed information on the fatigue testing results.

Figure 10 summarizes the results of the static tests. For both Aggregates A and E, it is clearly shown that Pavebond A.P. and the silane coupling agents reduced the indirect tensile strength of the asphalt concrete mixtures. An examination of the fractured faces indicated that less than 5% and from 10% to 25% coarse aggregate fracture was observed for specimens manufactured with Aggregates A and E, respectively. Since the primary failure mechanism was by debonding, this suggests that adhesion between the asphalt cement and aggregate was reduced due to the presence of the additives. It is not clear whether the differences between Aggregates A and E in strength were due to chemical or physical differences between the two aggregates. It is clear, however, that a price must be paid for achieving an increase in stripping resistance; i.e. the chemical antistripping agents partially inhibit rather than promote bonding in air-cured specimens.

The results for the fatigue tests are shown in Figures 11 to 13. Figure 11 summarizes the data from all tests in terms of stress ratio versus the logarithm of the number of cycles to failure. There are two main observations which should be eluded to. First of all, the fatigue life of all mixes appeared to be similar when using stress ratio on the verical axis. The scatter for each mixture was generally too large to allow for the detection of small differences in fatigue life due to the addition of an antistripping agent. The second important point is that the number of cycles to failure recorded in this study are considerably less than those reported in Reference [25]. This is attributed to the difference in the definition for failure. In this study failure corresponds to a stage of loading where a well-defined crack developed whereas in Reference [25] failure corresponds to a complete fracture of the specimen. Owing to the loading configuration and failure mode of asphalt concrete, a failed sample may still be capable of supporting the applied cycle load. The author prefers the definition adopted for this study, since it is based on the onset of failure.

Figures 12 and 13 summarize the fatigue data using applied maximum tensile stress on the vertical axis. This description of fatigue strength allows one to take into account the direct effect of the loading level on fatigue life. The main conclusion drawn from these figures is that both Pavebond A.P. and the silanes reduce fatigue life. The reduction in fatigue life is severer for specimens containing Aggregate A. Silanes do not increase fatigue life as suggested in Reference [5]. A close scrutiny of the data in Reference [5] indicates that the

claim of increased fatigue life due to silane treatment of aggregates may have been premature since the reported improvement in fatigue life is quite small when taking into account the amount of scatter in the data of this reference.

For each test series, it was observed that fatigue failure occured at a well-defined level of accumulated plastic deformation. This is significant from a theoretical point of view, since it suggests that it is possible to express asphalt concrete damage in terms of accumulated plastic deformation and that failure occurs at some "unique damage level". Furthermore a comparison of the accumulated plastic deformation histories of the specimens indicates that the differences in the number of cycles to failure for specimens of the same series, at a given load level, were due to differences in the composition of each sample. It was found that, if two samples failed at approximately the same number of cycles then their deformation histories were the same. The primary mode of failure for the coarse aggregate was due to debonding.

TABLE 6

RESULTS FROM JAPANESE PETROLEUM INSTITUTE STRIPPING TEST

(a) Distilled Water Testing Environment

Antistripping Agent	Application Mode	Stripping Pattern for Aggregate A	B	C	D	E
control	– –	4-1	1	1	4-1(2)	1
Pavebond	Additive	2	1	1	1	1
Lime	ST	1	1	1	–	–
Glymo	Additive	1	–	–	–	–
	ST	1	1	1	1	1
Damo	Additive	4-1	–	–	–	–
	ST	1	1	1	1	1
Octeo	Additive	4-1	–	–	–	–
	ST	1	–	–	1	–

(b) Salt Water Testing Environment

Antistripping Agent	Application Mode	Stripping Pattern for Aggregate A	B	C	D	E
control	– –	4-2	2	2	4-1(2)	2
Pavebond	Additive	2	1	1	1	1
Lime	ST	2	1	1	1	1
Glymo	Additive	2	–	–	–	–
	ST	1	1	1	1	1
Damo	Additive	4-2	–	–	–	–
	ST	1	1	1	1	2
Octeo	Additive	4-1(3)	–	–	–	–
	ST	1	–	–	1	–

Notes:

1. Fifty percent of aggregate has rating as identified by number enclosed in brackets.
2. Additive = stripping agent added to asphalt cement
   ST = surface treatment of aggregate.

TABLE 7

RESULTS FROM JAPANESE PETROLEUM INSTITUTE TEST ON GRASS SLIDES

Antistripping Agent	Application Mode	Area Stripped (%) CASE A	CASE B
control	– –	40	100
Pavebond A.P.	Additive	0	0
Lime	ST	0	0
Glymo	ST	0	0
Damo	Additive	0	50
	ST	50	100
Octeo	ST	10	0

Notes:

1. CASE A = slide cured at 25°C for 70 days
   CASE B = slide cured at 75°C for 24 hours
2. Additive = stripping agent added to asphalt cement
   ST = Surface Treatment of aggregate

TABLE 8

SUMMARY OF RESULTS FROM IMMERSION MARSHALL TEST*

Coarse Aggregate	Stripping Agent	Visual Assessment C	F	R	Marshall Stability(kN)	Retained Stability(%)
(a)	Specimens with Bow River Asphalt Cement					
A	---	3	2	9	24.4	51
	Glymo	0	2	5	28.2	49
	Damo	0	2	5	27.4	61
	Lime	0	2	5	26.2	68
	Pavebond	0	1	5	40.0	85
B	---	3	2	9	22.8	57
	Glymo	0	2	5	26.2	50
	Damo	0	2	5	25.4	54
	Lime	0	2	5	25.1	69
D	---	3	2	9	30.7	42
	Glymo	0	2	5	29.2	50
	Damo	0	2	5	28.0	55
	Lime	0	2	5	30.1	70
E	---	3	2	7	28.2	51
(b)	Specimens with Batch Plant Asphalt Cement					
E	---	1	2	7	33.9	37
	Damo(1)	0	2	7	33.1	63
	Damo(2)		6		30.4	75
	Damo(3)	2	1	7	23.1	102
	Damo(4)	3	1	8	24.8	87
	Pavebond	0	1	5	32.2	86

Notes:

1. R = Visual Stripping Rating: No stripping, R = 3
   Worst stripping R = 9
2. Stripping level in coarse aggregate, $0 < C < 3$.
3. Stripping level in fine aggregate, $0 < F < 2$.
4. (1) = only coarse aggregate treated with 3% of 1% silane solution.
   (2) = Fine and coarse aggregate treated with 3% of 1% silane solution.
   (3) = Fine aggregate treated with 9% of 1% silane solution, coarse aggregate treated with 3% of 1% silane solution.
   (4) = 0.9 percent silane was added to asphalt cement.

* All specimens were manufactured using the Campbellville fine aggregate.

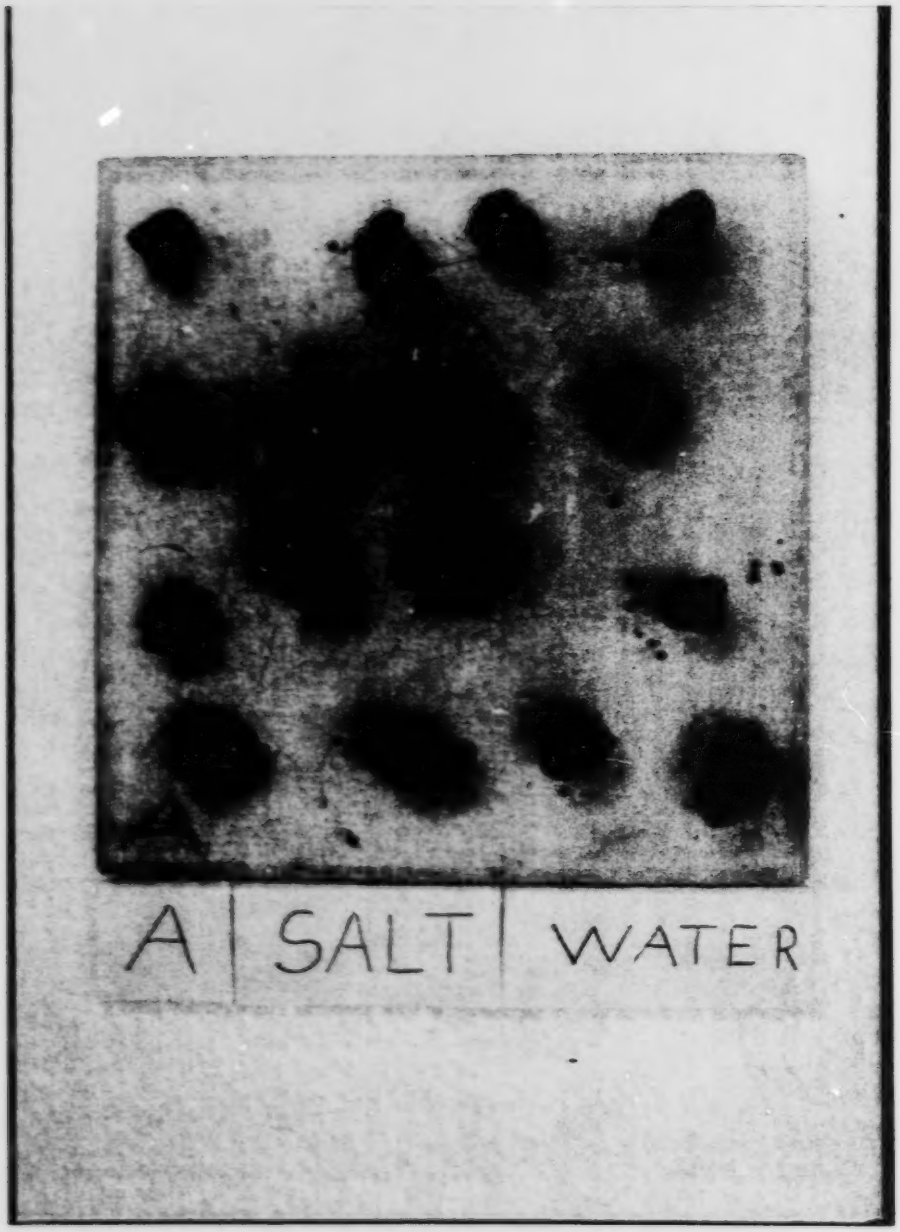


Figure 5/ Appearance of nontreated Aggregate A, which was coated with asphalt cement, after JPI test (salt water environment)

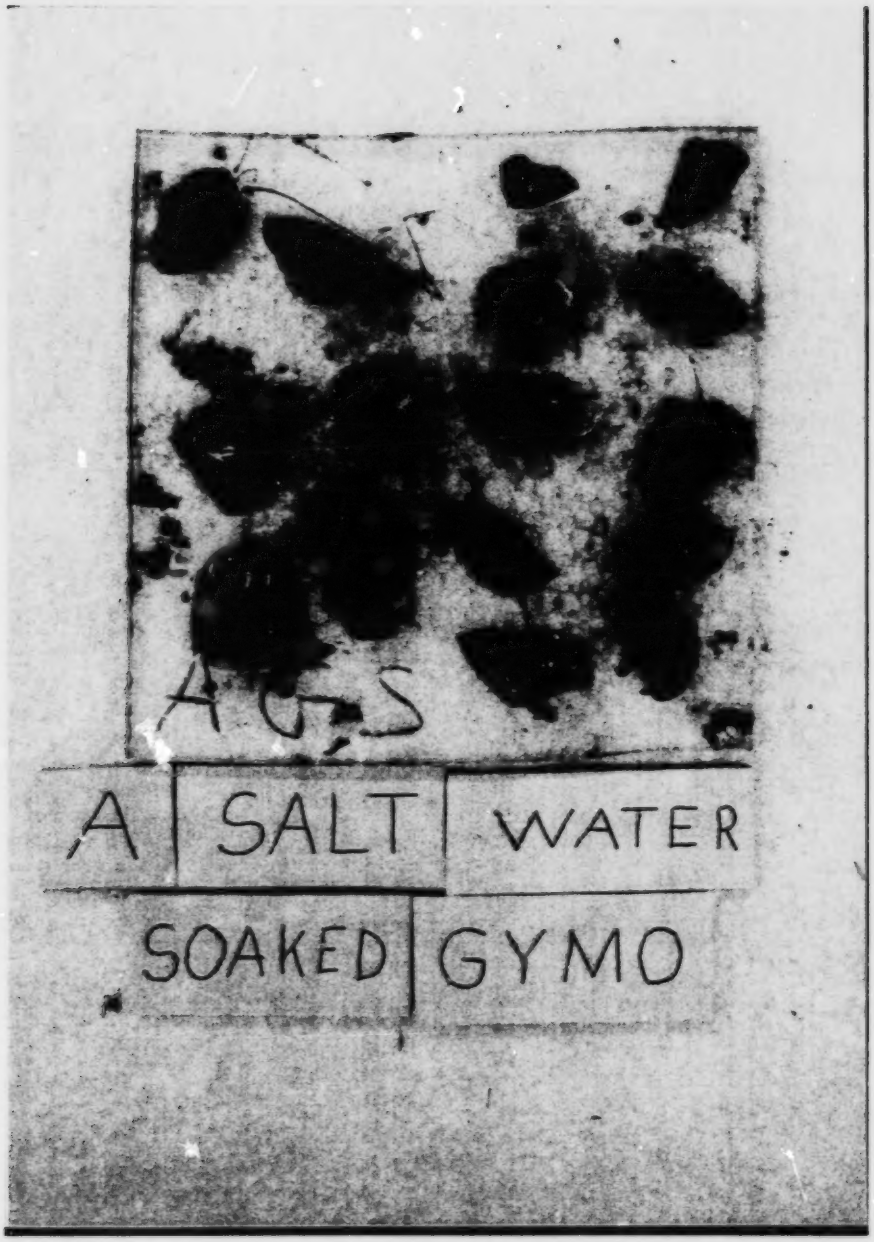


Figure 6/ Appearance of Glymo-treated Aggregate A, after JPI test (salt water Environment)

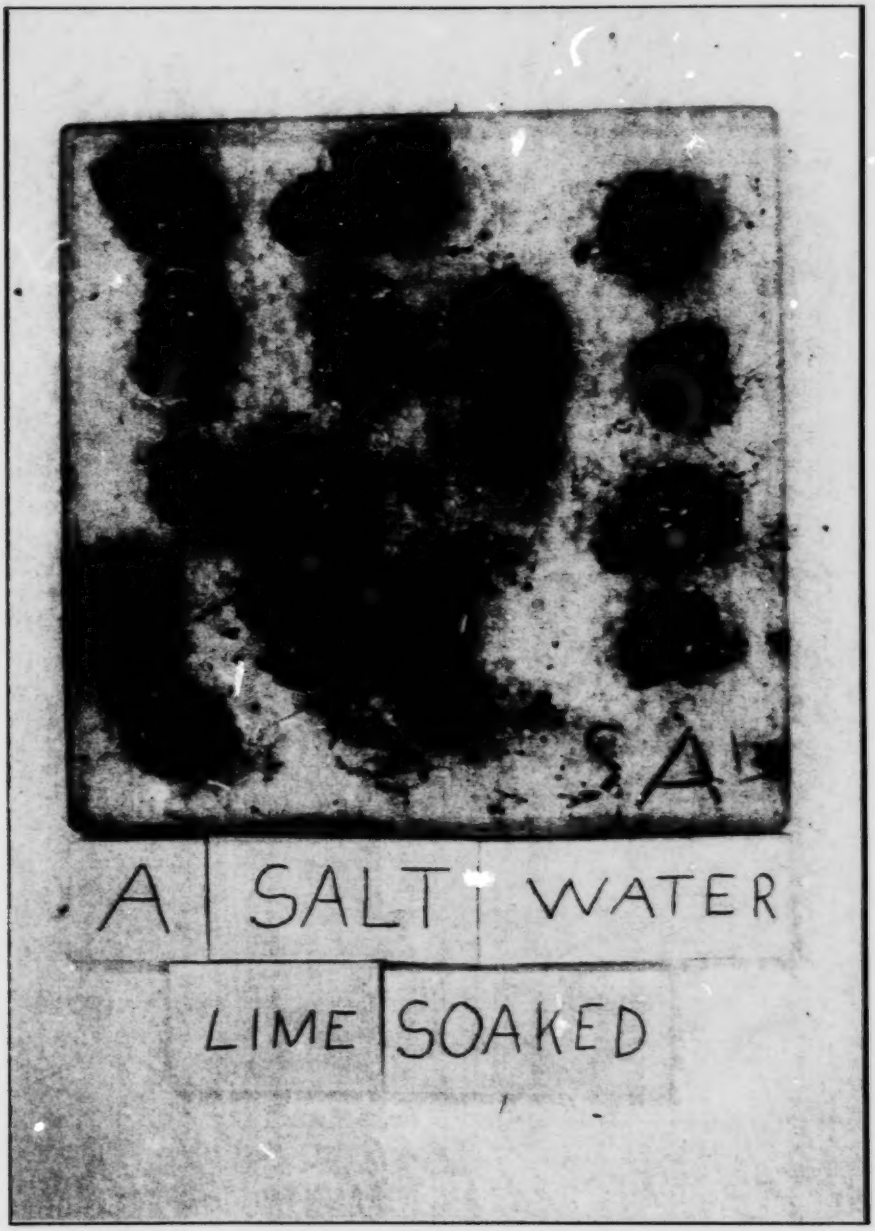


Figure 7/ Appearance of lime-treated Aggregate A, after JPI test (salt water Environment)

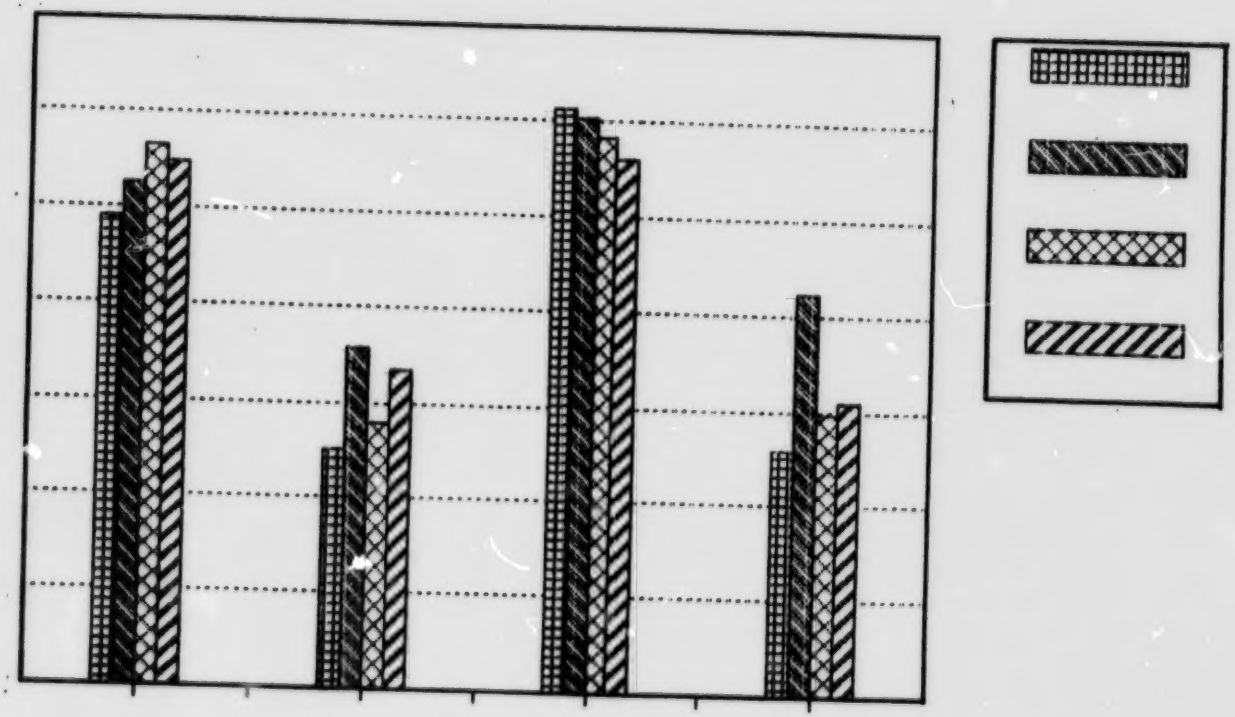


FIGURE 8. Immersion-Marshall test results of specimens manufactured using Campbellville sand and Bow River asphalt cement.

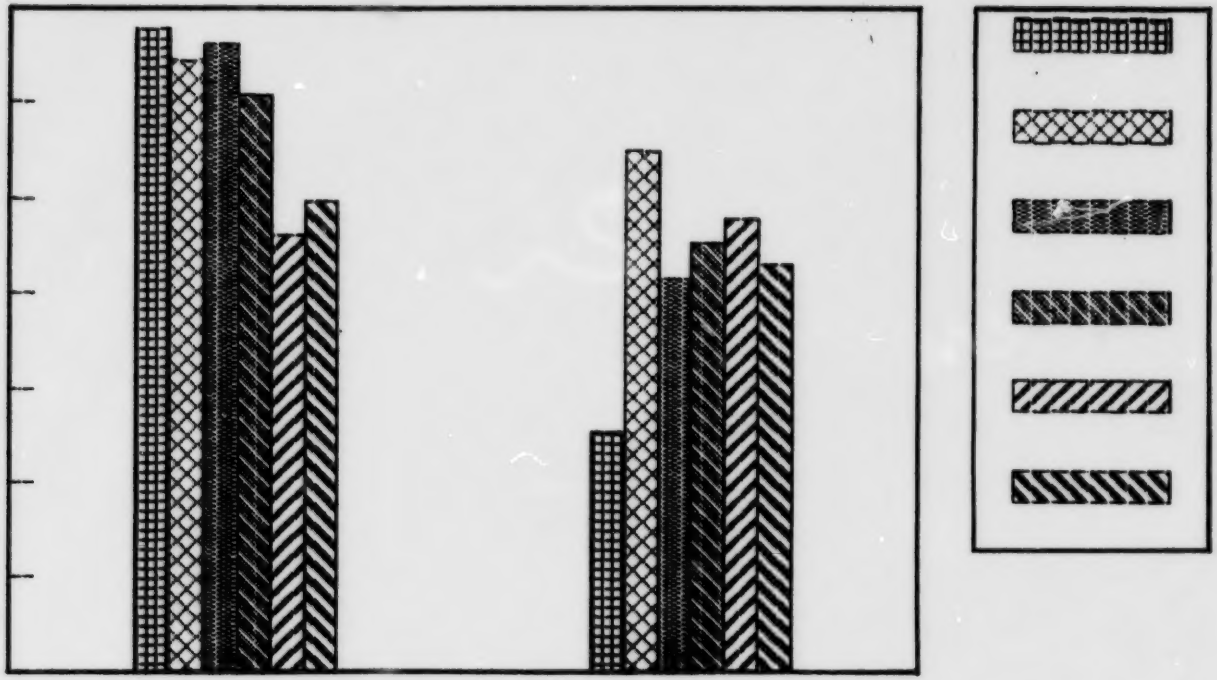


FIGURE 9. Immersion-Marshall test results of specimens manufactured using Aggregate E, Campbellville sand and batch plant asphalt cement.

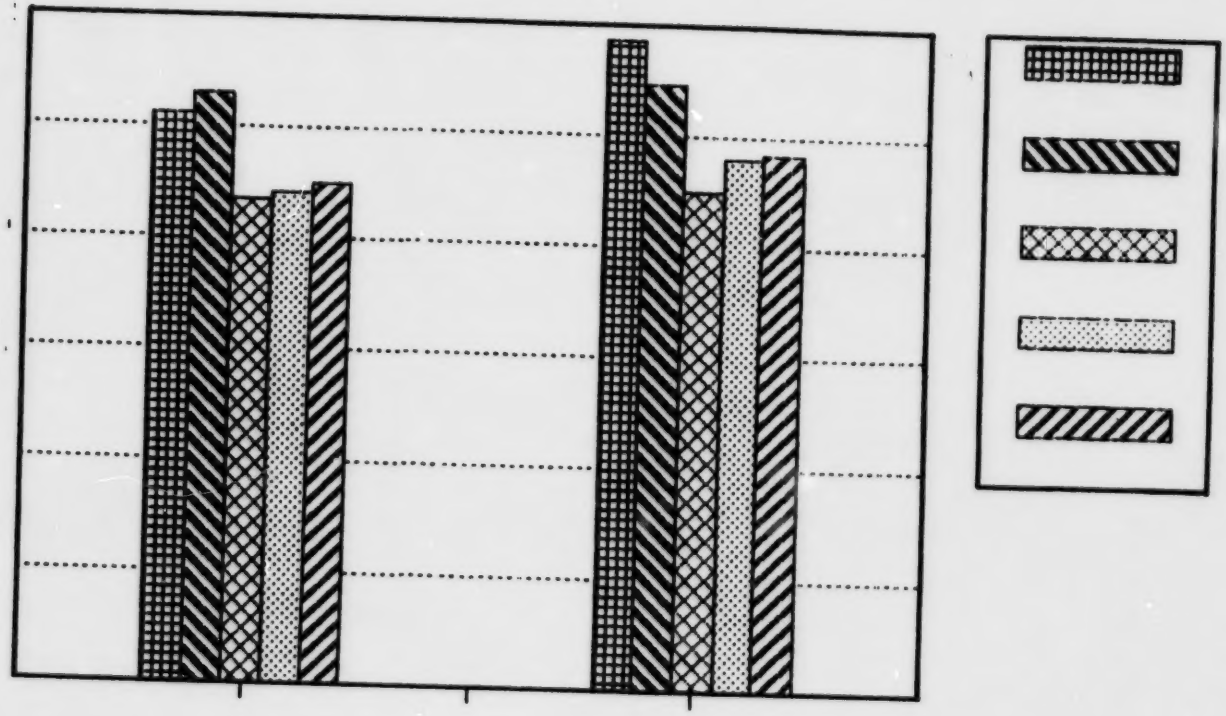


FIGURE 10. Average indirect tensile strength of fatigue test specimens manufactured using Campbellville sand and Bow River asphalt cement.

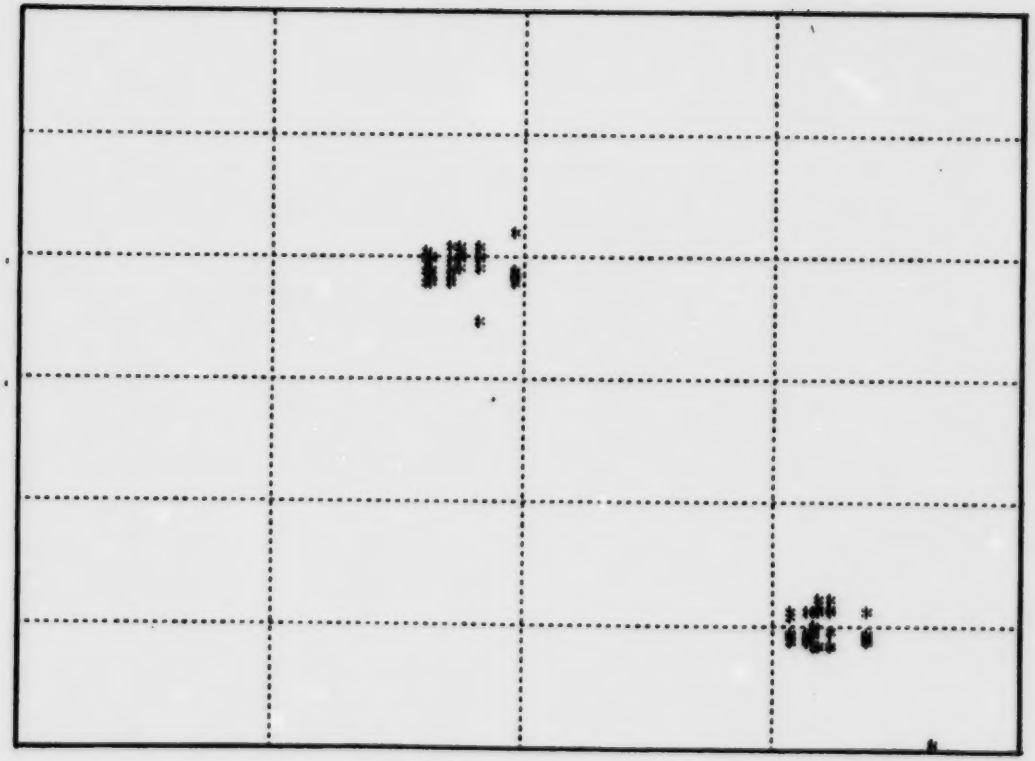


FIGURE 11. Summary of all fatigue test results in terms of stress ratio.

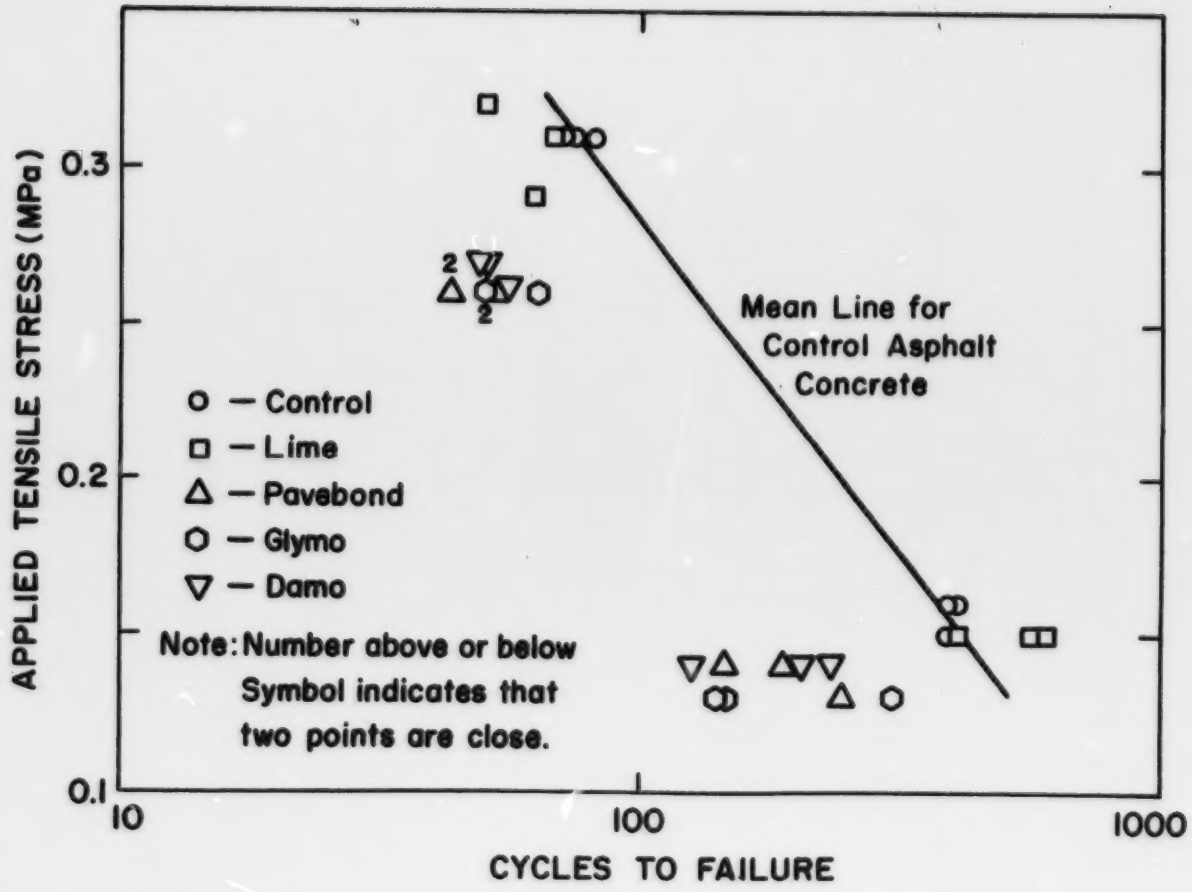


FIGURE 12. Summary of all fatigue test results for Aggregate A.

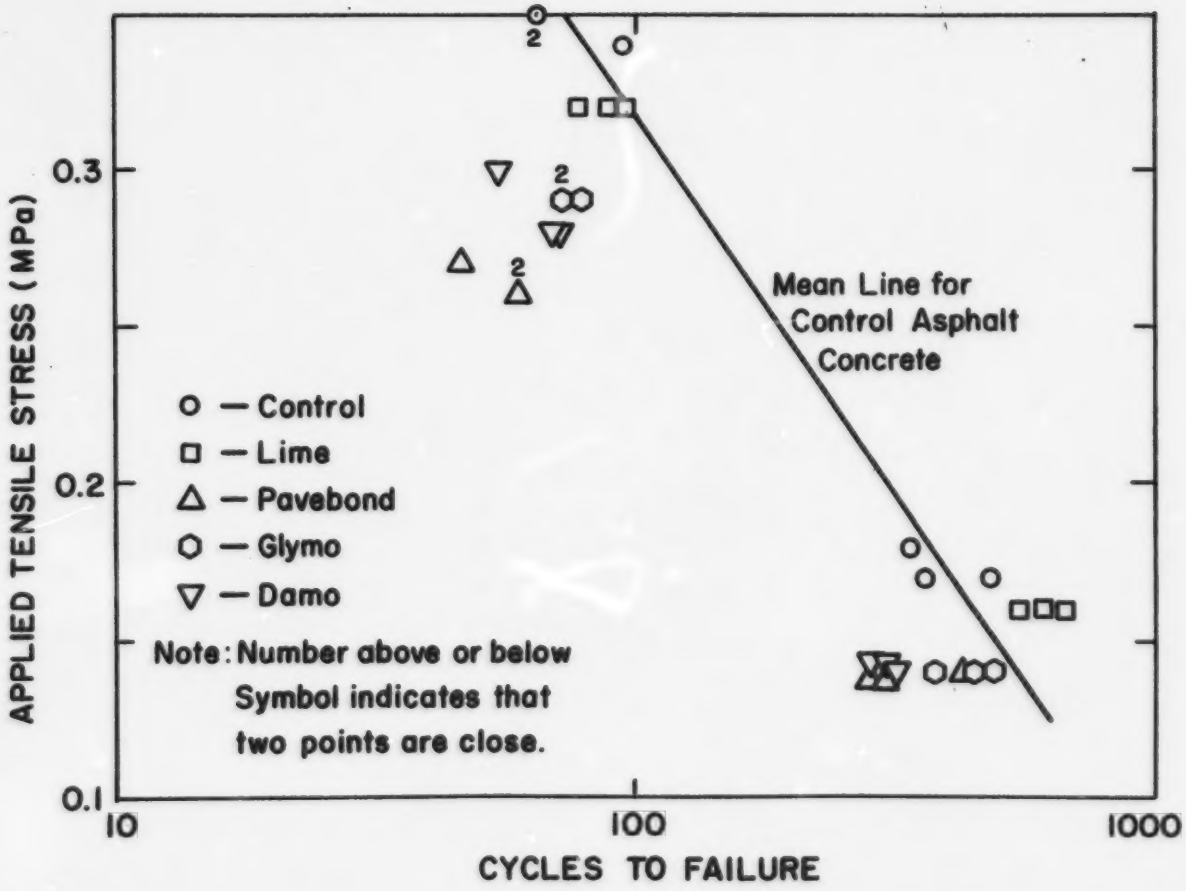


FIGURE 13. Summary of all fatigue test results for Aggregate E.

5.0 CONCLUDING REMARKS AND RECOMMENDATIONS

This report provided a brief literature review on stripping and on the use of silane coupling agents for improving the resistance of an asphalt concrete mix to stripping. It also described a testing programme which evaluated the effectiveness of silanes as antistripping agents for some Ontario aggregates, and investigated the notion that silanes may improve the fatigue life of asphalt concrete.

The main conclusions drawn from this study include:

1. based on the Japanese Petroleum Institute test, treatment of aggregates with silanes improves the compatibility between siliceous aggregates and asphalt cement;
2. surface treatment of aggregate with a silane is more effective than incorporating a silane as an asphalt cement additive;
3. Pavebond A.P. and hydrated lime are more effective in improving resistance to stripping than the silane coupling agents;
4. Pavebond A.P. and silane coupling agents reduce the tensile strength of air-cured asphalt concrete – both antistripping agents 'appear' to partially inhibit the development of strong asphalt cement-aggregate bonds; and
5. owing to a reduction in tensile strength, an asphalt concrete containing Pavebond A.P. or a silane coupling agent has a shorter fatigue life than an asphalt concrete containing lime or no additive.

It is clear from the results of this study that the treatment of the coarse aggregate alone will not bring about the desired improvement to the stripping resistance of an asphalt concrete mix if stripping is also due to the fine aggregate. Unfortunately, owing to a limited supply of the asphalt cement which was used for this study it was not possible to fully investigate the effect of treating the fine aggregate with silanes.

Since silanes appear to reduce the tensile strength of asphalt concrete, their use as an antistripping agent is not recommended. It is recommended that future research should emphasize:

1. studying the effect of antistripping agents on the fatigue life of asphalt concrete; and
2. developing more economical procedures for incorporating lime into asphalt concrete mixes.

The last recommendation is made since lime has a good record, when compared with those of other antistripping agents, with respect to improving resistance to stripping.

In conclusion, silane coupling agents do have the potential for reducing stripping. However, until it can be shown that pretreatment of aggregates with silane coupling agents or the use of silane asphalt cement additives can provide greater benefits than demonstrated by this study, it is recommended that contractors continue using the better antistripping agents currently available on the market.

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APPENDIX A

LITERATURE REVIEW

JEGEL

JEGEL 88117

SILANE COUPLING AGENTS TO REDUCE MOISTURE SUSCEPTIBILITY OF ASPHALT CONCRETE

APPENDIX A

STRIPPING IN ASPHALT CONCRETE LITERATURE REVIEW

With Emphasis on Mechanics, Causes and Prevention (Basics), Ontario Experience and Contract Requirements, Silane Coupling Agent Patents and Studies, Testing Methods, Limitations, Interpretation and Trends, and Alternate Antistripping Agents.

Prepared By

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(John Emery)

FOR

McMASTER UNIVERSITY
HIGHWAY MATERIALS LABORATORY

MAY 15, 1989

Given the extensive technical literature available on stripping in asphalt concrete, only selected references have been cited (each typically has its own reference list), except in the case of silane agents where all references found are cited. Key references were supplied to the Principal Researcher during the literature review.

STRIPPING IN ASPHALT CONCRETE
LITERATURE REVIEW

INTRODUCTION

This literature review of stripping in asphalt concrete, completed by John Emery Geotechnical Engineering Limited (JEGEL - John Emery, Principal Engineer), is based on: JEGEL experience with 'Ontario' asphalt technology; 232 technical abstracts from a DIALOG Transportation Research Information Service (TRIS) on-line search for [(asphalt or bituminous) and (stripping or antistripping)] (specific search selected after considering titles for a range of appropriate key works) [1]*; technical papers in JEGEL library supplemented by technical papers obtained on the basis of the TRIS abstracts; 23 patent abstracts from a DIALOG CLAIMS/U.S. Patent Files on-line search for (silane and asphalt) and (silane and stripping) [2], with the full Chevron Research Company 1977 Patent on surfacing compositions comprising aggregate, asphalt cement and aminoalkyl polyalkoxy-silanes [21] supplied by the Principal Researcher; and discussions with Don Fohs (Chief Materials Division, Federal Highway Administration, FHWA) to determine the current status of American silane coupling agents studies [3]. The references selected from the literature review of stripping in asphalt concrete are given by general topic at the end: sources [1-3]; Ontario Ministry of Transportation (MTO) and general agency experience [4-12]; studies on silane coupling agents [13-17]; patents on the use of silanes in asphalt concrete and related applications [18-31]; use of silanes as water repellant treatment [32]; general information on moisture susceptibility of asphalt concrete and antistripping agents [33-50]; testing [51-77]; and the use of lime as an antistripping agent [78-85].

MECHANICS, CAUSES AND PREVENTION OF STRIPPING IN ASPHALT CONCRETE

Asphalt concrete deterioration due to moisture susceptibility (stripping - breaking of the 'adhesive' bond between the aggregate surface(s) and asphalt cement, and/or softening - reduction of asphalt concrete cohesion, with stripping

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* See the list of references at the end.

of primary concern as a significant potential cause of distress [12,35-337,49, 79]) has been [33,35,36], and continues to be [34,36-40], of general concern to pavement engineers, including Ontario experience, research and current antistripping additive requirements [4-9,59,60], as supported by the extensive experience of other North American agencies [3,10-12].

It would appear that there are five basic types of stripping [35-37]:

1. emulsification (spontaneous emulsification) - asphalt cement can 'react' with free water to form an 'inverted' emulsion in the presence of certain additives (unfortunately, including some antistripping agents, particularly at 'high' dosages) and/or mineral clays;
2. detachment - asphalt cement is separated from the aggregate surface(s) by a thin layer of water with no obvious break in the asphalt cement coating (asphalt cement film can be peeled cleanly from the aggregate);
3. displacement - asphalt cement adhering to the aggregate surface(s) is removed and replaced by free water that gets to the aggregate surface(s) through a break(s) in the asphalt cement coating (incomplete coating during mixing and/or film rupture, etc.);
4. film rupture (stripping initiator) - asphalt cement film on aggregate surface(s) is ruptured during production/placement and/or traffic action, particularly at aggregate sharp edges and corners; and
5. 'hydraulic scour' and/or dynamic pore pressure? - movement of water in saturated asphalt pavement (surface courses) and/or pressure build up in trapped water under traffic action can contribute to stripping (technical literature generally quite vague on this).

From the above mechanics of stripping, it is clear that the cause of stripping in asphalt concrete is water getting between the asphalt cement film and aggregate surface(s) and replacing the asphalt cement that is critical to

asphalt pavement durability (cohesion) [36,37]. There is ample opportunity for water to get into asphalt concrete from: moisture in, or on, improperly dried aggregate; rainfall seeping through cracks, 'porous' pavement or shoulder; subsurface water seepage, if upward gradient; capillary water rising from the subgrade; and water vapour transmission through pavement structure. Factors influencing when and how the water then gets to the aggregate surface include [35-37]:

1. water in, or on, the dried aggregate - high water absorption and/or adsorption makes drying more difficult;
2. aggregate type - 'siliceous' aggregates more prone to stripping than 'carbonate' aggregates;
3. aggregate surface texture - 'smooth' surface texture less resistant to asphalt cement stripping than rough surface texture;
4. dust-coated aggregate (also combustion product coatings) - asphalt cement does not adhere and dust creates film defects (pinholes);
5. stockpile age - some newly crushed aggregates exhibit poor resistance to asphalt cement stripping;
6. spontaneous emulsification - antistripping agents can become stripping agents under certain conditions;
7. asphalt cement properties - the chemical and physical properties of each asphalt cement are unique, and can dramatically influence the stripping behaviour of an asphalt mix;
8. hot mix design, production and placement - high in place air voids, for instance, can promote water movements; and
9. free water availability to asphalt pavement structure.

An understanding of the mechanisms and causes of stripping in asphalt concrete can be used to develop guidelines for minimizing or preventing stripping, including [36,37]:

1. dense graded asphalt concrete - proper hot mix design (including assessment of antistripping agent requirements, if any), production (hot, dust free, dry aggregates, and aggregate particles completely and

uniformily coated with asphalt cement for instance) and placement (compaction - 6 to 8 percent in place air voids - important to both stability and durability, for instance);

2. open graded asphalt concrete - stripping is of more concern than for dense graded based on typical field performance [12], requiring careful consideration of all factors listed, particularly the hot mix design to ensure adequate asphalt cement film thickness (thick and even film) for durability, and positive pavement structure drainage;
3. provide positive pavement structure drainage - minimize water (moisture) ingress from all sources noting that stripping often starts from below in binder courses;
4. stockpile freshly crushed aggregates with poor stripping resistance - 'aging' often improves performance of aggregate (traprock in Southern Ontario, for instance);
5. select available aggregate(s) with highest resistance to stripping and/or incorporate as approved antistripping agent (compatible, heat stable, proper dosage, etc.), based on appropriate testing [MTO immersion Marshall test with plunger compacted air voids of about 8 percent and vacuum saturation, for instance [57]; and
6. ensure good quality control during all stages of asphalt pavement construction.

ONTARIO EXPERIENCE AND CONTRACT REQUIREMENTS

Ontario experience, based mainly on MTO studies that identified a stripping potential and consequent asphalt pavement durability concern for many aggregate sources [8 provides an excellent summary], has resulted in special provision, designated source material, testing and contract requirements for considering the potential stripping of aggregates in hot mix [4,5,57,58,60,78]. These can best be summarized directly from the new MTO Special Provision for contractor mix designs [60] -

"Stripping test LS-283 Method of Test for Resistance to Stripping of Asphalt Cement in Bituminous Mixture by Immersion Marshall shall be completed within

the mix design procedure to determine the need for and required amount of anti-stripping additive (a) when an aggregate is used which is on the Aggregates Sources List, (b) when an aggregate is used which is on the Aggregates Sources List and an anti-stripping additive is indicated as being required, (c) when an aggregate is used which is in the Manual of Designated Sources for Materials and an anti-stripping additive is indicated as being required, or (d) when an Aggregate Sources List is not provided and the aggregate source selected has a history of requiring an anti-stripping additive. The amount of anti-stripping additive required shall be sufficient to provide a minimum of 70% retained stability as determined by stripping test LS-283. The procedure for test LS-283 shall conform to the Ministry of Transportation Laboratory Testing Manual."

SILANE COUPLING AGENT PATENTS AND STUDIES

The DIALOG U.S. patent abstract search [2] clearly indicated that major chemical and asphalt companies (3M, Kao Soap, Chevron and Texaco) have completed studies/patented asphalt mixes incorporating a range of silanes as antistripping agents/adhesion promoters [19-23], but the main interest appears to be in the use of silanes for adhesion promotion in the coating of glass fiber with asphalts and construction products [24-32]. The exception to this appears to be Degussa in Germany who appear to be currently involved in very relevant studies/test sections/marketing? of silanes in asphalt concrete applications such as a bonding improvement additive in recycled mixes [17, information obtained supplied to Principal Researcher]. It would appear to be important to check for any potential patent problems if the research for the Ministry (MTO) results in actual hot mix applications for silanes in Ontario.

It is understood that the work of the Principal Researcher for the Ministry developed from interest in the very positive results for silane coupling agents (asphalt cement-aggregate surface adhesion promoters) reported in the 1987 Japanese PICA-3 paper "Improvement of Asphalt Pavement Durability by Surface Treatment of Coarse Aggregates" [16]. In fact, 'similar' studies have also been completed in the United States from about 1952 to recently [13-15,18], with

'mixed' results in terms of improved stripping resistance. This experience has been well summarized by comments from discussions with Don Fohs of the FHWA [3]: silanes are not good across the board for all aggregates with a stripping problem; hydrated lime is often the most effective antistripping agent; and it is important that all the hot mix components (coarse aggregate, fine aggregate, asphalt cement and antistripping agent) be assessed for representative asphalt concrete using an established procedure such as the Lottman test.

LABORATORY PROCEDURES TO ASSESS STRIPPING (MOISTURE DAMAGE) IN ASPHALT CONCRETE.

While it is important to have field inspection procedures to assess the extent of moisture damage (stripping) in asphalt pavements under actual service conditions (typically requires inspection/testing of cores as stripping often starts in binder course(s)), the focus of tests for moisture damage in asphalt concrete has been a range of laboratory procedures that have the purposes of: assessing the potential for stripping in an asphalt mix; determining the effectiveness of antistripping agents; identifying the component(s) (typically aggregate) 'responsible' for stripping; and establishing the extent of moisture damage (stripping) with service life (simulated and/or field samples) [test procedures - 51-63, studies/descriptions/applications/limitations of test procedures - 64-77]. Testing for stripping in asphalt concrete is of course made difficult by the many interacting factors that may influence moisture damage such as asphalt cement and aggregate (filler, fine and coarse) properties/ characteristics, hot mix design, hot mix production and placement and service conditions, particularly availability of moisture.

The two basic types of laboratory procedures for assessing the stripping potential of an asphalt concrete are: tests run on loose hot mix samples of asphalt cement coated aggregate components; and tests run on compacted asphalt concrete samples or cores from asphalt pavements [74]. Tests on loose hot mix samples or asphalt cement coated aggregate components typically involve moisture conditioning (static immersion, dynamic immersion, chemical immersion or boiling) and qualitative evaluation of the percent retained asphalt cement coating of the aggregate (MTO LS-285 "Method of Test for Stripping by Static Immersion" for

instance [58]. It would appear that the most widely used test on loose hot mix is the boiling test [Texas Boiling Test developed by Kennedy for instance [79]).

Tests on compacted asphalt concrete samples or cores are based on comparing a property such as tensile strength (moisture damage in asphalt concrete results in a substantial reduction in tensile strength from adhesion loss due to stripping and/or cohesion loss due to softening of asphalt cement matrix) before and after moisture conditioning. The indirect tensile test procedure with moisture conditioning ('Lottman procedure' -NCHRP 246 and Tunnicliff and Root NCHRP 274 [66,69]) has become the most widely used procedure and has been 'adopted' by AASHTO [56], SHRP [62] and ASTM [55]. The earlier, widely used, immersion compression [51] and immersion Marshall [57,59] procedures have not proven effective in predicting moisture damage in asphalt concrete unless the air voids in the compacted sample are representative of those anticipated in the field under service conditions, i.e. laboratory compaction procedure air voids of 6 to 8 percent as in the MTO immersion Marshall procedure [57] that is the 'required' Ministry test and the ASTM procedure [51] when modified this year [55].

While there is on-going research and debate between the 'Kennedy, boiling test/pedestal test' supporters and 'Lottman indirect tensile test' supporters which will not be continued here, it would appear that the FHWA, AASHTO and SHRP have satisfied themselves with the applicability of the Lottman procedure for predicting and monitoring moisture damage in asphalt concrete as indicated by the Abstract from Stuart's FHWA study on test procedures [75]:

> "Procedures for evaluating the moisture susceptibility of asphalt mixtures were compared by performing them on mixtures having a known history of susceptibility. Data included the retained ratios, visual stripping, mechanical values (tensile strength, stability, etc.), saturation, and swell. The most promising procedures appeared to be the NCHRP 246 and NCHRP 274. Moisture susceptibility was not effectively predicted by the 1-Minute Boiling Water, 10-Minute Boiling Water, Immersion-Compression, Marshall-Immersion, and Dynamic Tumbling procedures. The NCHRP 246 procedure (often

referred to as the Lottman procedure) contained two parts: one for short-term pavement performance, and one for long-term pavement performance. The short-term part was not found to be useful with regards to predicting performance. An 80-percent pass/fail criterion was chosen for both tensile strength ratios in the NCHRP 246 and NCHRP 274 procedures, and 70 percent for the M_r test. Ten percent or greater visual stripping generally indicated unacceptable damage in all procedures performed on compacted mixtures.

The data indicated that a freezing period, or higher air void levels, can be beneficial for evaluating moisture susceptibility. The degree of saturation was found to be important in that sufficient water must enter a specimen; however, saturation was not found to be the dominant factor affecting moisture damage. The effects of saturation were masked by other mechanisms such as the type of mechanical test, air void levels, and freezing. There was no conclusive evidence that high saturations or oversaturation due to vacuum conditioning adversely affected the test results."

It is also pertinent to note from Stuart's work [75], that with a borderline hot mix an antistripping additive may produce a 'passing' asphalt concrete without any improvement in the quality of the hot mix by decreasing the dry tensile strength and/or increasing the wet tensile strength, and it is also possible that the visual stripping may decrease without a change in the wet tensile strength or the retained strength ratio.

ALTERNATE ANTISTRIPPING AGENTS

During the literature review on stripping in asphalt concrete, there were a number of references found on the comparative efficacy of chemical lime (typically hydrated lime) as an antistripping agent, its regular use by many agencies, and apparent additional benefits of increased asphalt concrete stiffness and reduced age hardening of asphalt cement [78-85]. For instance, it would appear that hydrated lime has been found to be more effective as an antistripping agent than organo functional silane and commercial heat-stable

liquid antistripping agents in research by Kennedy [18]. For this reason, it would appear that research on the cost-effective introduction of chemical lime at hot mix plants where an antistripping agent is required [80,85], and the use of chemical lime in open graded asphalt mixes (OFC) to reduce moisture damage [82], may provide significant benefits to improved asphalt pavement durability.

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83. Stroup-Gardiner, M. and Epps, J., Four Variables That Affect the Performance of Lime in Asphalt-aggregate Mixtures, Transportation Research Record 1115, Transportation Research Board, Washington, D.C., 1987.

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85. Thaler, T., Lime test could lead to lower paving costs, Canadian Construction Record, September 1988.

APPENDIX B

SELECTION OF SILANE ADHESION PROMOTERS AS CANDIDATES FOR AN ASPHALT PAVING STUDY

ORTECH

INDUSTRIAL MATERIALS TECHNOLOGY CENTRE

Adhesives and Sealants

SELECTION OF SILANE ADHESION PROMOTERS AS CANDIDATES FOR AN ASHPHALT PAVING STUDY

Report No.
A&S 352-88-69-41208

September 8, 1988

For

Department of Civil Engineering & Engineering Mechanics
McMaster University
Hamilton, Ontario
L8S 4L7

Attention: Dr. D. Stolle

ORTECH
INTERNATIONAL
2395 Speakman Drive
Mississauga, Ontario L5K 1B3
(416) 822-4111 (800) 268-5390
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Report No. A&S 352-88-69-41208
For McMaster University

INTRODUCTION

The Department of Civil Engineering and Engineering Mechanics at McMaster University is involved in a project to evaluate coupling agents, or adhesion promoters, to reduce stripping problems in asphalt road paving. A report at a recent Paving in Cold Areas (PUCA) conference indicated some success in this area using silane coupling agents. The Adhesives Group at ORTECH has been asked to recommend up to three such coupling agents for evaluation in a testing program.

DISCUSSION

Silane coupling agents are used in a broad range of applications to obtain improvements in adhesion between two substrates. These coupling agents make use of dual functionality to produce this improvement, in many cases bonding chemically to both substrates, thereby altering the surface that is "see" by the other substrate. One "end" of the molecule is hydrolyzable and can react with moisture, typically absorbed on a filler or supplied externally, to form siloxane bonds with the filler surface, and the other end is chosen to react if possible with the binder. Although there are dozens of different silanes used as coupling agents, many of them can be represented by the general formula

where R is methyl or ethyl, and X is the reactive group at the end of a short hydrocarbon chain R', often propyl.

In thermoset resins, choice of the silane can be made on chemical grounds, as X can be an epoxy, amine, vinyl, methacryloxy etc.

group which will take place in the polymerisation or cross-linking reaction, so that the coupling agent froms chemical bonds to both the filler and the binder, which accounts for the dramatic improvements in physical properties of, say, glass filled plastics.

For thermoplastics, such as asphalt, the choice is not as clear, as no chemical reaction takes place at the organic end. However, the organic end should be compatible with (if soluble in) the binder phase. Asphalt presents a few additional problems in that being a natural product its composition is a mixture of various chemical types, and in varying proportions.

SELECTION

The selections presented below have been made after literature and product reviews, and after discussions with silane producers. Samples have been obtained from one manufacturer and have been presented together with this Report. (Major suppliers are listed in the Appendix). Rather than make absolute selections, however, three categories of coupling agent have been chosen, two of these having alternate selections. This leaves the final choice with the principal researchers, and this may be based on odour, toxicity or other such handling related properly or on cost.

The three categories were chosen as follows:

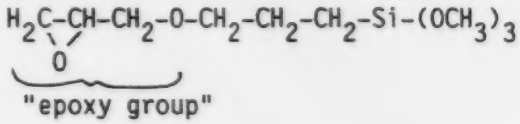
1) One of the two silanes tested fully in the study presented at the PICA conference, for comparative purposes.

2) A silane coupling agent containing an amine group, since amines are used currently as antistripping agents in asphalt.

3) Since asphalt is a mixture of organic compounds, a silane with a strictly hydrocarbon chain (i.e. no reactive functionality) was chosen on the principal of solution compatibility.

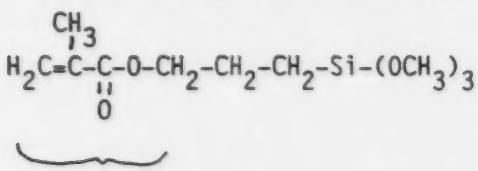
More specifically, the silanes in the three categories are the following.

1) (a) 3 - glycidoxypropyltrimethoxysilane (GLYMO)



This is the "epoxy" silane in the PICA reports.

(b) 3-methacryloxypropyltrimethoxysilane (MEMO)



This is the erroneously named "vinyl" silane in PICA report; there is a vinyl group on the end but it is part of the methacrylate group. This could more accurately be described as an "acrylic" silane.

2) (a) 3-aminopropyltriethoxysilane (AMEO)

$NH_2-CH_2-CH_2-CH_2-Si-(OCH_2CH_3)_3$

This is the "amino" silane in the PICA report, which was not tested to the extent of the two above.

(b) N-(2-aminoethyl-3-aminopropyl)Trimethoxysilane) (DAMO)

$$NH_2-CH_2-CH_2-NH-CH_2CH_2CH_2-Si-(OCH_3)_3$$

This contains two amino groups, and a longer hydrocarbon chain, and may therefore be more effective than AMEO.

Amines have a distinctive odour, which may be offensive to some. This was a comment made about AMEO in the PICA report, although in that case the AMEO was added to the hot asphalt, which presumably increased the level of the odour. Of the two amino silanes, DAMO has a higher boiling point, and higher flashpoint.

3) n-octyltriethoxysilane (OCTEO)

$$C_8\ H_{17}\ Si(OC_2\ H_5)_3$$

Contains a linear chain of eight carbon atoms (CF n-octane with a siloxy group on one end).

APPLICATIONS

The silanes are all clear, low viscosity, relatively involatile liquids, and can be applied in either of two ways; by treatment of the aggregate prior to mixing with the asphalt, or by direct addition to the asphalt. Treatment of the aggregate can be by spraying, tumbling etc., of the aggregate with a low concentration (1-2%) solution, and then drying. Since the silane forms chemical bonds with the aggregate, the aggregate can be treated prior to mixing with the asphalt without special care in subsequent handling or transporting. Concentration of the silane in the final asphalt mix should be about 0.1%, so assuming an approximately 5/95 asphalt/aggregate ratio this requires 0.1% by weight of filler.

SOLUTION STABILITY

The fact that the silane reacts with surface moisture on a filler implies that its stability in water is limited. The reaction with water liberates alcohol (methanol from methoxysilanes etc.), so that addition of alcohol to an aqueous solution is a way to prolong the stability of such solutions by reducing the chemical drive for the degradation reaction. This will of course, add to the cost of raw materials and handling of the solution. According to the supplier of the samples, however, the two amino-silanes (AMEO, DAMO) have very good stability as 5-10% aqueous solutions (AMEO almost indefinitely). The other silanes require a pH adjustment to pH 3-5 to minimize their stability. The shortest shelf life for such a solution of the supplied samples is estimated to be 48 hours for MEMO. This may not be a problem if solutions are to be made daily for use during that day only. (The useful lifetime of a solution can be estimated as the time to the first appearance of a white precipitate in the solution).

ECONOMICS

The cost of using one silane compared to another has many factors:

- basic raw material cost.
- cost of other chemicals (e.g. alcohol, acid) to produce a useable solution.
- stability of the solution, i.e. how often it has to be discarded and renewed.

Raw Material Costs

The price (in U.S. dollars as of August 9, 1988) per pound, for

7-12 drum lots is as follows:

1 (a)	GLYMO	$10.40	
1 (b)	MEMO	11.45	
2 (a)	AMEO	7.80	Tech. grade 7.35
2 (b)	DAMO	9.80	Tech. grade 7.20
2	OCTEO	6.25	

This will increase the cost of 1 ton of asphalt by approximately C$ 18-34.

Other Chemical Costs and Solution Stability

From the discussion on solution stability above, it is clear that acid will be required for the pH adjustment of GLYMO, MEMO or OCTEO. Hydrochloric acid should suffice, and is relatively cheap. (25 cents/lb.). The other costs of using coupling agents will depend on how the application takes place, and how this is managed. Direct addition of asphalt would be straight forward, and spraying or otherwise wetting the aggregate would require a calculation of the amount required for use that day, to minimize losses from having to discard unused material. If the practice involves a daily solution make-up, then alcohol would not be required to stabilize the solutions. Drying the aggregate may also introduce additional costs.

TOXICITY AND SAFE HANDLING

Silanes

The silane coupling agents are all water-like liquids with flashpoints well above room temperature and high boiling points (See Table).

	Boiling Pt, (°C/mm Hg)	Flashpoint (°C)
GLYMO	120°/2	135°
MEMO	78°/1	92°
AMEO	122°/30	96°
DAMO	140°/15	121°
OCTEO	98°/2	100°

Material Safety Data Sheets for each silane are appended to this Report. Generally these compounds are mild to severe eye, skin and inhalation irritants, and are toxic if injested. This toxicity is mainly due to the silane reacting with moisture in the mucons membranes, producing the effects of the alcohol produced. The alcohol will also be liberated during the drying of treated aggregate, so precautions for the use of alcohol and its vapours should be in effect.

Acid

Hydrochloric acid is most conveniently purchased in its most concentrated form, and so usual precautions for handling concentrated acids should be applied. (For pH adjustment, use of dilute solutions is more convenient as well as being safer).

It is recommended that the use of splash-proof goggles and impervious rubber gloves be the minimum precautions taken during handling either of the above chemicals.

CONCLUSIONS

A review of silane coupling agents for use as anit-stripping agents in asphalt for road surface has resulted in five compounds being recommended for a final choice in three categories using the abbreviations introduced in the Report, the choices are:

1) GLYMO or MEMO - the former is slightly cheaper, less toxic, possible more stable in solution, has higher flashpoint and boiling point. MEMO showed slightly better anti-stripping results in the PICA report.

2) AMEO or DAMO - the former is cheaper (but not for the technical grade), has better solution stability, although DAMO's should also be good. DAMO is less toxic, has a higher flashpoint and boiling point. Because of its two amino groups and larger organic part, DAMO would be favoured in this category.

3) OCTEO - the only recommendation in this category, is also the cheapest of the five, so may do well as far as performance/cost ratio is concerned.

Ted Rozum
Project Technologist
Adhesives and Sealants

John Flack, Ph.D.
Section Manager
Coatings, Adhesives and Inks

APPENDIX

The samples and most of the information relating to the selected silane coupling agents were obtained from:

Huls America, Inc.
Petrarch Systems,
2570 Pearl Buck Road
Briston, PA
19007

Phone: (215) 781-9255
Lisa Westerfield.

Other major manufacturers of silane coupling agents are:

Dow Corning Corporation
Midland, M.I.
48686-0994

Union Carbide Corporation
Adhesion Promoters
270 Park Avenue
New York, NY
10017

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44-R1387

MATERIAL SAFETY DATA SHEET

[redacted]

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

CAS# 2943-75-1

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
[redacted]	(215)781-9255
ADDRESS (Number, Street, City, State and ZIP Code): 2731 BARTRAM ROAD BRISTOL, PA. 19007	
CHEMICAL NAME AND SYNONYMS: OCTYLTRIETHOXYSILANE	TRADE NAME AND SYNONYMS: 09835
CHEMICAL FAMILY: ORGANOSILANE	FORMULA: $C_{14}H_{32}O_3Si$

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)
n-OCTYLTRIETHOXYSILANE (NOT A SPECIFICATION)	≥95	1000 ppm*

SECTION III - PHYSICAL DATA

BOILING POINT (°F.)	98°C (2) torr	SPECIFIC GRAVITY (H_2O=1)	0.88
VAPOR PRESSURE (mm Hg.)		PERCENT, VOLATILE BY VOLUME (%)	>50%
VAPOR DENSITY (AIR=1)	>1	EVAPORATION RATE (Ether =1)	<1
SOLUBILITY IN WATER	Reacts Slowly		
APPEARANCE AND ODOR	CLEAR, COLORLESS LIQUID, SLIGHT ALCOHOL ODOR		

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	Uel
100°C (CLOSED CUP)			

EXTINGUISHING MEDIA
CARBON DIOXIDE, SAND, FOAM, DRY CHEMICAL - $NaHCO_3$ TYPE

SPECIAL FIRE FIGHTING PROCEDURES
FIREFIGHTERS SHOULD WEAR FULL PROTECTIVE CLOTHING INCLUDING A SELF-CONTAINED BREATHING APPARATUS.

UNUSUAL FIRE AND EXPLOSION HAZARDS
NONE

*BASED ON ETHANOL

(Continued on reverse side)

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
1000 ppm (BASED ON ETHANOL)

EFFECTS OF OVEREXPOSURE
MAY IRRITATE SKIN AND EYES. ETHANOL INHALATION: HEADACHE, IRRITATION OF EYES, NOSE, THROAT.

EMERGENCY AND FIRST AID PROCEDURES
SKIN: FLUSH WITH WATER. INHALATION: REMOVE TO FRESH AIR. EYES: FLUSH WITH WATER FOR 15 MINUTES, OBTAIN MEDICAL ATTENTION.

SECTION VI - REACTIVITY DATA

STABILITY			CONDITIONS TO AVOID
	UNSTABLE		REACTS SLOWLY WITH WATER TO PROVIDE ETHANOL
	STABLE	XX	

INCOMPATABILITY *(Materials to avoid)*
REACTS WITH WATER, ACIDS, ETC.

HAZARDOUS DECOMPOSITION PRODUCTS
SiO_2, CO_2 AND TRACES OF INCOMPLETELY BURNED CARBON PRODUCTS

HAZARDOUS POLYMERIZATION			CONDITIONS TO AVOID
	MAY OCCUR		
	WILL NOT OCCUR	XX	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
ELIMINATE SOURCES OF IGNITION. COVER SPILL WITH ABSORBENT MATERIAL SUCH AS SAWDUST OR SAND. SCOOP UP AND PLACE IN AN APPROPRIATE CONTAINER.

WASTE DISPOSAL METHOD
WASTE MATERIAL MAY BE INCINERATED IN ACCORDANCE WITH FEDERAL, STATE, AND LOCAL ENVIRONMENTAL REGULATIONS.

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION *(Specify type)*
ORGANIC VAPOR TYPE

VENTILATION			
	LOCAL EXHAUST	RECOMMENDED	SPECIAL
	MECHANICAL *(General)*	RECOMMENDED	OTHER

PROTECTIVE GLOVES	EYE PROTECTION
RUBBER OR PLASTIC	SAFETY GLASSES OR GOGGLES

OTHER PROTECTIVE EQUIPMENT

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
DO NOT STORE NEAR FOOD AND BEVERAGES

OTHER PRECAUTIONS
NOT FOR FOOD OR DRUG USE.

Form OSHA-20
Rev. May 72

[redacted]

MATERIAL SAFETY DATA SHEET CAT.NO.:G6720: 240

[redacted]
2731 BARTRAM ROAD
BRISTOL, PA 19007

EMERGENCY PHONE NUMBERS: CHEMTREC (800)424-9300; PETRARCH (215)781-9255

I. NAME AND PRODUCT

CATALOG NUMBER: G6720
CHEMNAME: Glycidoxypropyltrimethoxysilane; GLYMO; DYNASYLAN (R) GLYMO

CAS REG.NO.: 02530-83-8 FORMULA: C9H20O5Si

II. HAZARDOUS INGREDIENTS

COMPONENT	ACGIH TLV	OSHA PEL
Glycidoxypropyltrimethoxysilane (95%)	NA	NA

SARA Title III Section 313 Toxic Chemicals, if present, are indicated by (+) and are potentially at the maximum concentration listed.
SARA Title III Section 302 Extremely Hazardous Substances are indicated by (++).
CERCLA Hazardous Substances are indicated by (+++).

III. PHYSICAL DATA

APPEARANCE: Clear liquid

B.PT.(deg.C/mm): 120/2 VAPOR PRESSURE(mm/deg.C): NA
M.PT.(deg.C): NA

VAPOR DENSITY(AIR=1): >1 % SOLUBLE IN WATER: Reacts
SPECIF.GRAVITY: 1.070 % VOLATILE BY VOLUME: <50

IV. FIRE AND EXPLOSION HAZARD

FLASH POINT(TAG): 135° C. (closed cup)
FLAMMABLE LIMITS (STP IN AIR)
LOWER LIMITS: NA
UPPER LIMITS: NA

FIRE EXTINGUISHING MEDIA: Water, CO2, foam, dry chemical

PERSONAL PROTECTION FOR FIGHTING FIRE: Fire fighters must wear positive pressure breathing apparatus and full protective clothing.

V. REACTIVITY DATA

STABILITY (UNDER NORMAL CONDITIONS): Stable
CONDITIONS TO AVOID:
Contact with water or moist air. Generates methanol;TLV(skin,TWA)=200ppm
Contact with oxidizing agents. Contact with alkali & acid.

HAZARDOUS POLYMERIZATION: Will not occur
CONDITIONS TO AVOID: NA

HMIS RATINGS (Scale 0-4)
HEALTH: 2 FLAMMABILITY: 1 REACTIVITY: 1

VI. SPILL OR LEAK PROCEDURES

IN CASE OF SPILL:Absorb material with chemical binder and shovel absorbent into suitable container
Flush spill area with large amounts of water

DISPOSAL METHOD:Incinerate following all federal, state and local regulations

VII. HEALTH HAZARD DATA

TOXICITY:
Glycidoxypropyltrimethoxysilane:
Toxicity Data; orl-rat LD50: 23 g/kg; skn-rbt LD50: 3970 mg/kg.
Irritation Data; skn-rbt 500 mg (open) MLD IRR; eye-rbt 100 mg MLD IRR.

ROUTES AND EFFECTS OF EXPOSURE:
EYES: Moderately irritating. Harmful. Avoid contact.
SEE NOTE(S) BELOW.
SKIN: Moderately irritating. May be harmful. Avoid contact.
SEE NOTE(S) BELOW.
INHALATION: *Irritant. Pulmonary toxin.
SEE NOTE(S) BELOW.
INGESTION: *Irritant. Toxic.
SEE NOTE(S) BELOW.

NOTE:
Material may form a siloxane polymer on the skin, eyes, or in the lungs.
In the event of direct contact of the liquid with these tissues, seek medical attention.

NOTE:
Material generates Methanol(toxic) on contact with water or moisture on the skin, eyes, and mucous membranes.
Methanol is a tissue irritant that may be absorbed through the skin and produce systemic toxic effects. Vapors may be inhaled and metabolized to Formaldehyde and Formic acid resulting in systemic acidosis, blindness, and ultimately death from respiratory arrest. Liquid produces effects similar to inhalation overexposure when ingested.

FIRST AID PROCEDURES:
EYES: Flush with clean water for at least 15 minutes and consult physician
!!! GET MEDICAL ATTENTION IMMEDIATELY!!!

SKIN: Scrub with soap and water
SKIN: Remove contaminated clothing and shoes

INHALATION: Remove victim to fresh air. If not breathing use artificial respiration. If symptoms persist, get medical attention

INGESTION: Give one full cup of milk or water. Induce vomiting
INGESTION: Get medical attention

If symptoms persist, get medical attention

CARCINOGEN STATUS: NTP?: No IARC MONOGRAPH?: No OSHA REGULATED?: No

VIII. SPECIAL PROTECTION INFORMATION 240

VENTILATION:Local exhaust recommended
Mechanical ventilation required

RESPIRATORY PROTECTION: Use chemical cartridge respirator with appropriate cannister(s)

PROTECTIVE CLOTHING:Use impervious gloves

EYE PROTECTION: Use chemical goggles

IX. PRECAUTIONS OR OTHER COMMENTS

HANDLING AND STORAGE:Store in a cool and dry place
Maintain tightly closed container
Protect from moisture
Store away from alkaline materials
Store away from acidic materials
Store away from oxidizing materials
Provide adequate ventilation

D.O.T. NAME: Chemicals, n.o.s.
D.O.T. ID NO.: NA
D.O.T. LABEL: None

Since empty containers retain product residue, follow hazard precautions even after container is emptied.

NA = No applicable or relevant information available

(R) = Registered Trade Mark

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DATE: 06/21/88 REV.0

[redacted]
2731 BARTRAM ROAD
BRISTOL, PA 19007

: ENERGENCY : CHEMTREC (215)781-9255
: PHONE :
: NUMBERS : PETRARCH (215)781-9255

I. NAME AND PRODUCT

NAME: A0750
SYNONYMS: 3-Aminopropyltriethoxysilane

CAS REG.NO.: 919-30-2 FORMULA: $H_2N(CH_2)_3Si(OC_2H_5)_3$

II. HAZARDOUS INGREDIENTS

COMPONENT	ACGIH TLV	OSHA PEL
3-Aminopropyltriethoxysilane	NA	NA

III. PHYSICAL DATA

B.PT.(deg.C/mm): 68/3 VAPOR PRESSURE(mm/deg.C): 1psia
M.PT.(deg.C): NA APPEARANCE: Clear liquid

VAPOR DENSITY(AIR=1): >1 % SOLUBLE IN WATER: Reacts
SPECIF.GRAVITY: 0.95 % VOLATILE BY VOLUME: <50%

IV. FIRE AND EXPLOSION HAZARD

FLASH POINT: 205F

FLAMMABLE LIMITS (STP IN AIR)
LOWER LIMITS: NA
UPPER LIMITS: NA

FIRE EXTINGUISHING MEDIA: CO2, foam, dry chemical

PERSONAL PROTECTION FOR FIGHTING FIRE: Fire fighters must wear positive pressure breathing apparatus and full protective clothing.

V. REACTIVITY DATA

STABILITY (UNDER NORMAL CONDITIONS): Stable
CONDITIONS TO AVOID: Contact with water.

HAZARDOUS POLYMERIZATION: Will not occur
CONDITIONS TO AVOID: NA

HMIS RATINGS (Scale 0-4)

HEALTH: 3 FLAMMABILITY: 1 REACTIVITY: 1

VI. SPILL OR LEAK PROCEDURES

IN CASE OF SPILL:Absorb material with chemical binder and shovel absorbent into suitable container

DISPOSAL METHOD:Incinerate following all federal, state and local regulations

VII. HEALTH HAZARD DATA

TOXICITY:Oral rat LD50 1780mg/kg

ROUTES AND EFFECTS OF EXPOSURE:
EYES: Corrosive-causes tissue destruction. Conjunctivitis, corneal damage.

SKIN: Corrosive-causes tissue destruction.

INHALATION: No information available-Avoid contact.

INGESTION: Toxic.

FIRST AID PROCEDURES:
EYES: Flush with clean water for at least 15 minutes and consult physician

SKIN: Scrub with soap and water
Remove contaminated clothing and shoes

INHALATION: Remove victim to fresh air. If not breathing use artificial respiration. If symptoms persist, get medical attention

INGESTION: Do not induce vomiting
INGESTION: Get medical attention

If symptoms persist, get medical attention

CARCINOGEN STATUS: NTP?: NO IARC MONOGRAPH?: NO OSHA REGULATED?: NO

VIII. SPECIAL PROTECTION INFORMATION

VENTILATION:Maintain adequate ventilation

RESPIRATORY PROTECTION:Use gas mask with organic vapor cannister

PROTECTIVE CLOTHING:Use impervious gloves
Use impervious clothing as necessary to protect against skin contact

EYE PROTECTION:Chemical goggles required.

IX. PRECAUTIONS OR OTHER COMMENTS

HANDLING AND STORAGE:Store in a cool and dry place
Protect from moisture
Store away from acidic materials

D.O.T. NAME: Corrosive liquid n.o.s.
D.O.T. ID NO.: UN1760
D.O.T. LABEL: Corrosive

Since empty containers retain product residue, follow hazard precautions even after container is emptied.

==========

DATE: 7/22/87 REV.0 CC

NA = No applicable or relevant information available
(R) = Registered Trade Mark

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APPENDIX C

TABLE C.1

RESULTS FROM GRAIN SIZE ANALYSIS

Sieve Size	Sand	Percent Passing				
		A	B	C	D	E
12.5 mm	100.0	40	79.4	98.2	55.8	77.0
9.5 mm	100.0	0	9.9	70.5	0.6	4.3
No. 4	98.7		0	6.2	0	0
8	91.1			0		
16	79.1					
30	57.7					
50	26.9					
100	7.0					
200	2.5					

APPENDIX D

D.0 JAPANESE PETROLEUM INSTITUTE TEST FOR STRIPPING

D.1 Procedure [5]

1. Samples of a coarse aggegate are taken using 10 mm and 13 mm sieves. Fine particles on the surface of the coarse aggregate are washed out. They are put into an electric oven, until their weight becomes constant.

2. Twently pieces of the dried coarse aggregate are selected at random. They are put into an electric oven for 1 hour. The temperature is kept at 5°C higher than mixing temperature.

3. Asphalt is heated to mixing temperature.

4. Asphalt is added to the hot aggregate. The weight of the asphalt is $5.5 \pm 0.2\%$ of the weight of the coarse aggregate. The aggregate and asphalt are mixed using a heated spatula, until the aggregate is completely covered with asphalt.

5. The asphalt-coated aggregate is put on a glass plate. The size of the plate is 20x20 cm. The aggregate pieces should not touch each other.

6. The aggregate on the plate is put into hot water kept at 80°C. It is immersed in the hot water for 30 minutes.

7. The aggregate and the glass plate are transferred into room temperature water. An examiner observes the stripping pattern through the water's surface. The patterns are classified into the patterns shown in Figure 2.

APPENDIX E

IMMERSION MARSHALL TEST

E.1 Stripping Rating of Water-Cured Specimens (R)
(MTO Procedure L-283)

For laboratory prepared specimens the stripping rating R is calculated as

$$R = P + C + F$$

a)	Stripping Penetration:	No stripping evident	P = 3
		Stripping evident	P = 4
b)	Coarse Aggregate:	Percent stripped	
		- 10	C = 0
		10 - 30	C = 1
		31 - 60	C = 2
		61 -	C = 3
c)	Fine Aggregate:	0 - 10	F = 0
		11 - 30	F = 1
		31 -	F = 2

TABLE E.1

RESULTS FOR SPECIMENS USING BOW-RIVER ASPHALT CEMENT

Coarse Aggregate	Anti-Stripping Agent	G	Voids (%)	Air-Cured VMA (%)	Air-Cured Flow (.01")	Air-Cured Stability (kN)	Water-Cured Flow (.01")	Water-Cured Stability (kN)	R (-)
a) Campbellville Sand									
A	–	2.24	9.9	21.7	28	24.4	30	12.5	9
	Glymo	2.26	7.6	19.5	28	28.2	28	13.9	5
	Damo	2.24	8.6	20.4	24	27.4	28	16.7	5
	Lime	2.24	8.9	20.8	26	26.2	28	17.9	5
	Pavebond	2.30	9.4	12.3	28	40.0	30	34.0	5
B	–	2.29	6.2	18.4	25	22.8	31	12.9	9
	Glymo	2.29	7.8	19.8	25	26.2	7	13.2	5
	Damo	2.27	7.3	19.3	24	25.4	27	13.8	6
	Lime	2.28	7.7	19.8	28	25.1	24	17.4	5
D	–	2.27	7.6	19.6	26	30.7	32	12.9	9
	Glymo	2.27	7.3	19.2	26	29.2	30	14.8	5
	Damo	2.26	7.9	19.9	28	28.0	29	15.5	5
	Lime	2.28	7.2	19.2	27	30.1	29	21.2	5
E	–	2.29	8.4	20.5	25	28.2	28	14.2	7
b) Aberfoyle Sand									
A	–	2.24	7.24	19.1	26	29.9	31	11.5	8
	Lime	2.25	7.25	19.3	27	34.9	36	9.8	6
	Pavebond	2.24	7.74	19.6	26	33.9	31	18.8	6
	Octeo	2.24	7.69	19.6	27	36.2	34	7.7	6
	Octeo*	2.23	7.55	19.3	25	34.5	35	12.4	6

Notes:
1. G = Specific Gravity; VMA = Void Mineral Aggregate
2. Water curing was for 24 hours at 60°C (in tap water).

*Both coarse and fine aggregate were treated with silane coupling agent.

TABLE E.2

RESULTS FOR SPECIMENS INCORPORATING BATCH PLANT ASPHALT CEMENT AND CAMPBELLVILLE SAND

Coarse Aggregate	Anti-Stripping Agent	G	Voids (%)	Air-Cured VMA (%)	Air-Cured Flow (.01")	Air-Cured Stability (kN)	Water-Cured Flow (.01")	Water-Cured Stability (kN)	R (-)
E	–	2.30	7.8	20.0	23	33.9	24.5	12.6	7
	Damo(1)	2.30	6.1	18.2	23	33.1	24.4	20.8	6
	Damo(2)	2.31	6.6	18.8	21	30.4	24.0	22.7	6
	Damo(3)	2.31	5.57	17.7	23	23.1	25.0	24.0	7
	Damo(4)	2.30	6.58	18.7	22	24.8	23.0	21.5	8
	Pavebond	2.30	6.3	18.5	22	32.2	23.1	27.5	5

Notes:
(1) = only coarse aggregate treated with 3% of 1% silane solution
(2) = fine and coarse aggregate treated with 3% of 1% silane solution
(3) = fine aggregate treated with 9% of 1% silane solution, coarse aggregate treated with 3% of 1% silane solution
(4) = 0.9% silane was added to asphalt cement

APPENDIX F

SUMMARY OF INDIRECT TENSILE RESULTS

TABLE F.1

STATIC FAILURE DATA

Antistripping Agent	Specific Gravity	Voids (%)	Width (mm)	Failure Load (kg)	Tensile Stress (MPa)
a) Aggregate A					
–	2.40	5.1	66	1020	0.95
	2.43	4.1	62	1130	1.12
	2.42	4.5	65	1060	1.00
Lime	2.39	3.3	65	1110	1.05
	2.40	3.1	68	1120	1.07
	2.39	3.4	68	1160	1.05
Pavebond	2.37	4.3	67	980	0.90
	2.37	4.2	67	920	0.84
	2.35	5.0	66	920	0.86
Glymo	2.40	5.6	64	850	0.82
	2.40	5.6	63	960	0.94
	2.40	5.6	61	870	0.88
Damo	2.42	5.0	65	960	0.91
	2.41	5.3	65	880	0.83
	2.41	5.4	65	1030	0.97
b) Aggregate E					
–	2.42	4.9	61	1160	1.17
	2.42	4.8	63	1250	1.22
	2.42	5.1	63	1130	1.10
Lime	2.41	3.9	65	1190	1.13
	2.40	4.2	65	1120	1.06
	2.41	3.9	67	1190	1.09
Pavebond	2.37	5.5	67	940	0.86
	2.37	5.4	67	1110	1.02
	2.37	5.5	67	900	0.83
Glymo	2.43	4.5	64	920	0.88
	2.44	4.1	65	1090	1.03
	2.42	4.7	63	1000	0.98
Damo	2.40	5.6	464	1020	0.98
	2.41	5.2	63	1060	1.03
	2.41	5.0	64	950	0.91

TABLE F.2

FATIGUE FAILURE DATA, AGGREGATE A

Antistripping Agent	Specific Gravity	Voids (%)	Width (mm)	Cycles to Failure	Applied Load (kg)	Tensile Stress (MPa)
–	2.42	4.5	63	81	314	0.31
	2.43	4.2	62	71	315	0.31
	2.42	4.3	63	74	315	0.31
	2.42	4.4	63	412	160	0.16
	2.42	4.3	66	380	160	0.15
	2.43	4.0	63	391	160	0.16
Lime	2.41	2.7	67	62	320	0.29
	2.40	2.8	64	68	320	0.31
	2.40	3.0	62	50	320	0.32
	2.40	2.7	62	563	150	0.15
	2.41	2.7	63	604	150	0.15
	2.40	2.9	62	408	150	0.15
Pavebond	2.36	4.7	65	52	270	0.26
	2.35	4.9	64	43	270	0.26
	2.35	4.9	63	43	270	0.26
	2.35	4.8	63	147	140	0.14
	2.36	4.4	64	245	140	0.13
	2.36	4.8	65	189	140	0.14
Glymo	2.4	5.6	63	50	270	0.26
	2.4	5.6	65	63	270	0.26
	2.4	5.6	64	51	270	0.26
	2.38	6.3	63	140	130	0.13
	2.39	6.1	63	146	130	0.13
	2.39	5.9	59*	304	130	0.14
Damo	2.41	5.3	63	49	280	0.27
	2.41	5.3	65	55	280	0.26
	2.41	5.1	63	51	280	0.27
	2.41	5.1	62	203	140	0.14
	2.41	5.3	62	227	140	0.14
	2.40	5.5	62	126	140	0.14

TABLE F.3

FATIGUE FAILURE DATA, AGGREGATE E

Antistripping Agent	Specific Gravity	Voids (%)	Width (mm)	Cycles to Failure	Applied Load (kg)	Tensile Stress (MPa)
–	2.41	5.2	62	64	352	0.35
	2.42	5.1	61	65	350	0.35
	2.42	5.1	64	96	350	0.34
	2.41	5.4	64	369	181	0.17
	2.43	4.8	66	486	180	0.17
	2.42	5.1	63	341	180	0.18
Lime	2.41	3.8	65	78	340	0.32
	2.42	3.5	64	96	340	0.32
	2.42	3.6	64	89	340	0.32
	2.41	4.0	63	665	160	0.16
	2.41	4.1	62	608	160	0.16
	2.41	3.9	62	550	160	0.16
Pavebond	2.36	5.6	66	59	280	0.26
	2.36	5.6	64	46	280	0.27
	2.38	5.1	65	60	280	0.26
	2.36	5.7	63	272	140	0.14
	2.39	4.5	62	433	140	0.14
	2.38	4.9	63	301	140	0.14
Glymo	2.43	4.3	61	73	290	0.29
	2.43	4.2	63	71	290	0.28
	2.44	4.1	63	79	290	0.28
	2.43	4.2	61	377	140	0.14
	2.43	4.2	61	490	140	0.14
	2.44	4.1	61	443	140	0.14
Damo	2.41	5.3	64	73	290	0.28
	2.41	5.4	63	70	290	0.28
	2.40	5.7	60	55	290	0.30
	2.40	5.5	60	287	140	0.14
	2.42	4.9	60	314	140	0.14
	2.41	5.3	60	321	140	0.14